SYMPOSIUM F
Nanophase and Nanocomposite Materials III

November 29 – December 2, 1999

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*Invited paper
8:30 AM #P1.1 SUCCESSFUL STRATEGIES FOR FINDING NICHE FOR THE RARE USEFUL NANOCOMPOSITES: CUTTING TOOLS AND NITRIDE POWDER SYNTHESIS. Bastum Roy, Evan Pugh Professor of the Solid State Emeritus, Materials Research Laboratory, The Pennsylvania State University, University Park, PA.

As the eldest champion of nanocomposites one is disappointed that few major developments of materials with radically improved properties have resulted in well over a decade. This paper will examine the emergence of the existence of nanocomposites in nature (specific minerals in special forms) or in technology (many glasses and the entire glass-ceramic industry) to guiding research in finding useful nanocomposites. One key strategy for making useful nanocomposites is the use of microwave radiation for reaction and sintering. Two examples will be described utilizing nanocomposites in the use of microwave radiation for reaction and sintering: (1) by reducing the reaction time by one order of magnitude in WC-Co cutting tools (Agrawal et al.), and (2) by utilizing excimer laser reactions in a unique configuration using the Penn State microwave process to make nanophase AIN, TiN, VN etc. (Budzynan et al.).

9:00 AM #P1.2 MAGNETIC ENTROPY CHANGE OF NANOCOMPOSITES COMPOSED OF A SINGLE MATRIX AND GRANES OF IRON OXIDE@NITRIDE. T.T. Yasuoka, K. Nakahama, T. Nakajima, M. Katsuji, T. Nakayama and K. Nishihara, Osaka Univ., Osaka, JAPAN.

Magnetoceric effect of superparamagnetic nanocomposites composed of iron-oxide or iron-nitride grains dispersed in a matrix was studied by calculating magnetic entropy change $\Delta S$ induced by a change in magnetic field $H$ applied to the material. These nanocomposites were synthesized by the inert gas condensation technique and nitridation by heat treatment in an ammonia gas stream. Average sizes of the iron-containing grains were 10-30 nm. Magnetic phases in the materials were $Fe_3O_4$ or $\gamma$-Fe$_2$O$_3$ for the oxide-composites and $\delta$-$Fe_3N$ or $\delta$-$Fe_3N$ for the nitride-composites. The superparamagnetism was confirmed typically in a temperature range from room temperature to 150 K. Values of the $\Delta S$ were obtained by applying a thermodynamic Maxwell’s relation, ($\Delta S/\theta_0$) = ($\Delta M/\theta$)$_H$, to the data of magnetization $M$ measured at various temperatures $\theta$. These results clearly indicated significant enhancement due to the nanocrystal structure. The values of the $\Delta S$ were investigated by comparing their dependences on temperature and magnetic field with those given by the Langevin’s superparamagnetism, which showed a fair agreement in a nanocomposite with 95% Fe while a considerable disagreement in another one with 50% Fe.


With the growing interest in nanomaterials and nanostructured materials, established technologies are beginning to use nanomaterials instead of conventional materials, and new applications are evolving that exploit the unique properties of nanomaterials. In particular, novel applications are emerging for the use of nanoparticle dispersions as a second phase. The matrix containing the nanoparticles can be either a liquid, polymer, metal or a ceramic. However, the morphology of the dispersed phase is not the same in different applications. For example, in the area of chemical mechanical polishing, the ‘aggregate’ particle size in the liquid medium has to be tailored into the nanoscale. On the other hand, for extrinsic electrical conductivity in polymers and in liquid rechargeable battery electrodes, the primary nanoparticles need to be processed so as to deliberately form micron size aggregates with an open structure (fractal morphology). The aggregated nanoparticles are then dispersed in a polymer or processing media in the applications mentioned above, and the corresponding properties and performance of these ‘novel’ nanocomposites will be discussed.

9:30 AM #P1.4 INFLUENCE OF PARTICLE SIZE ON THERMAL RESIDUAL STRESSES ON ABRASIVE WEAR OF ALUMINA/SIC NANOCOMPOSITES. J.L. Ortiz-Merino, R.E. Field, University of Oxford, Department of Materials, Oxford, UNITED KINGDOM.

Alumina/SIC nanocomposites consist of alumina grains of conventional size (a few um), containing a dispersion of SiC ‘nanoparticles’ (0.18nm). The nanocomposites have improved mechanical and tribological properties compared to unreinforced alumina. This paper shows that the abrasive wear rate of alumina-based nanocomposites can be reduced by a factor of three or more compared to unreinforced alumina of the same grain size. The improvements were the result of the suppression of surface grain pullout on the addition of the nanoparticles. Correlation of the response to abrasion with systematic changes in microstructure and thermal residual stress showed that these effects were dependent on the alumina grain boundaries which were responsible for reduction of grain pullout, and that the effect was most pronounced for systems in which the thermal residual stresses were highly compressive in the particles. These conclusions were supported by modelling of the tribo-erosion process, which showed that the compressive residual stresses around the nanoparticles could cause significant local toughening of the grain boundaries.


Surface residual stresses induced by grinding and polishing in alumina/silicon carbide nanocomposite and monolithic alumina have been investigated by Hertzian indentation and fluorescence spectroscopy. Specimens were ground and then polished with diamond slurry with grit size ranging between 8 µm and 1 µm. The results show that the surface residual stress state in the nanocomposites is more sensitive to surface treatment than that in the monolithic alumina. Surfaces of both ceramics were examined in cross-section by TEM so as to make direct observation of the plastic deformation induced by the surface treatments. There is a change in the predominant deformation micromechanism from twinning in the alumina to dislocation generation in the nanocomposites.

10:00 AM #P1.6 PREPARATION AND FUNCTIONALITY OF NANOCOMPOSITE FILMS COMPOSED OF COBALT OXIDE ULTRAFINE PARTICLES. Naoto Koshinski, Tatsuki Suzuki, Quan Li, Nat. Inst. Mater. Sci. Res., Tsukuba, JAPAN.

Nanocomposites that consist of oxide nanoparticles dispersed in other oxide matrices would have a great potential for a new type of functional materials, because various kinds of functional oxides can be combined to create novel functional properties. One of the examples for such functional nanocomposites is a CoO/SiO$_2$ nanocomposite that has been developed in our group. The nanocomposite structure plays an important role in the reversible optical transmission change observed by a magnetic field change from air to nitrogen oxide. However, most of combinations for oxide/oxide composites are easy to form compounds or solid solutions, which resulted in the unavailability of various nanocomposite structures and the difficulty in controlling their microstructure. In the CoO/SiO$_2$ nanocomposite system, in this paper, the ArF excimer laser ablation technique to obtain monodisperse crystalline oxide nanoparticles not under island structure formation scheme at the initial stage of film growth but under inert gas condensation scheme is described. The effects of preparation condition on the size, morphology and crystallinity of nanocomposites and nanoparticles aggregated films were extensively studied mainly for cobalt oxide. Utilizing the suitable nanoparticle preparation conditions, we can obtain nanoparticle-aggregated films that can be crystallized at comparatively lower temperature than those obtained by the conventional method. The preparation of nanocomposite films with the material combinations that cannot be obtained by simultaneous deposition method becomes possible by alternate deposition technique. The structural characteristics of these films with nanoparticle preparation conditions will be described.

11:00 AM #P1.7 THERMITE REACTIONS IN AI/CoO$_2$, NANOCLAYMATE FOILS. Kerri J. Bleiweis, Michael E. Breis, Tim P. Wells, The Johns Hopkins Univ., Dept. of Materials Science & Eng., Baltimore, MD.

In a typical thermite reaction, Al powder is used to reduce Fe$_2$O$_3$ powder and the heat released is sufficient to melt the resulting Fe product. This reaction has been used to join materials for nearly 100 years, but it is not yet well understood. Here,
we consider a similar reaction between Al and CuO in nanocomposite films which provide unique opportunities to study thermite reactions in nanometer-sized systems. Sample powders were prepared in a high vacuum chamber and sputter deposited at ambient temperature and they contain many alternating nanocrystalline layers of Al and CuO, with the total film thickness being ten of tens of microns. The thermite reactions are easily ignited by using a laser to localize heat propagation very rapidly down the film. We will present reaction velocity measurements using an optical technique and heats of reaction quantified using differential scanning calorimetry (DSC). We will also isolate and identify intermediate reaction phases from ongoing experiments and X-ray diffraction and transmission electron microscopy. Based on these measurements, we will present insights into the diffusion mechanisms and reaction kinetics of thermite reactions in these nanocomposite materials. We will also highlight potential applications, including the joining of microscale circuit board components that are too small to facilitate the use of powders.

11:15 AM F1.8
PULSED LASER DEPOSITION OF GALLIUM ARSENIDE NANOSTRUCTURES AND THIN FILMS BY A COPPER-VAPOR LASER
Laurie L. Davies, W. W. Hsu, W. W. O’Driscoll, D. C. Boebinger, Lawrence Livermore National Laboratory, Livermore, CA; J.A. Reimer, Lawrence Berkeley National Laboratory and Department of Chemical Engineering, University of California, Berkeley, CA.

The properties of GaAs nanocrystals and films deposited on substrates by a Cu-vapor laser were investigated. Nanocrystals of GaAs were produced by laser ablating a GaAs target in an Ar background gas. X-ray diffraction and transmission electron microscopy revealed that these GaAs nanocrystals had randomly oriented crystalline cores and As-rich amorphous oxide shells. These clusters assembled, upon vacuum annealing, along step edges and at defects to form three-dimensional structures. Our results also showed that GaAs films deposited in vacuum were not crystalline and rich in As. Post-deposition annealing in vacuum to between 400°C and 500°C drove off the excess As. The stoichiometry of the film was confirmed by both Auger electron spectroscopy and x-ray photoelectron spectroscopy.

11:30 AM F2.0
THE MICROSTRUCTURE AND PROPERTIES OF FRAMEWORK ZIRCONIUM PHOSPHATES BASED NON-COMPOSITES.

Nanocomposites comprised of highly dispersed zirconia loaded with tungsten and platinum are known to be among the most promising catalysts of CS-C7 alkanes isomerization. However, their properties strongly depend upon the starting component - amorphous hydrated zirconia prepared by various procedures, making performance unpredictable. In this work, as alternative to zirconia, nanosized crystalline framework zirconium phosphates synthesized via sol-gel route or mechanochemical activation of the mixture of solid starting salts followed by hydrothermal treatment in the presence of polyethylene oxide were used. Acid properties of zirconium phosphates were tuned by incorporation of substituting cations (Li, Al, B, W) or metallic P into the lattice at the preparation stage. Nanoparticles/clusters of WOx were introduced either during mechanochemical activation stage or via traditional impregnation route followed by calcination. Ps (up to 0.3%) was supported from home-made zirconium phosphates. XPS, TPR, EXAFS, UV-VIS, FTIR, XPS, TPR, were used to characterize the nanocomposites structure/microstructure and surface properties. The density of Lewis and Bronsted acid centers and their strength were evaluated using FTIR of surface hydroxyl groups in adsorbed CO and ESCA spectroscopy of adsorbed TEMP oxide molecule. Nanocomposites performance in the reactions of pentane and hexane hydrogenation were characterized both in pulse and flow regimes, and for some systems, the whole profile of data is available. Cracking was effectively suppressed. Catalytic properties of nanocomposites were analyzed from the microstructural and mechanistic point of view taking into account distribution of carbocarbonogen in the isomerization and hydrogenation reactions and the resulting functional groups between spatially separated components. This work is in part supported by the University of Russian Program under Grant No 354.

11:45 AM F1.10
MAGNETOTHERMIC ELECTROCHEMICAL DEPOSITION OF NANOCOMPOSITE THIN FILMS. J. L. King and Y. Xing, Department of Chemical Engineering, Johns Hopkins University, Baltimore, MD.

A novel magnetophoresis electrochemical deposition method employing a magnetic field gradient during electrodeposition to produce nanocomposites composed of magnetic nanoparticles in a thin film matrix will be discussed. Magnetic iron oxide nanoparticles with a mean size of less than 50 nm are dispersed in an electrolyte solution containing copper sulfate and sulfuric acid. Under a subject magnetic field gradient, these particles are embedded into a copper thin film matrix as it is being electrochemically deposited. The as-deposited composite. With a thin copper film, films containing a large density of nanoparticles have been fabricated with up to 50% particle volume fraction. These nanocomposite films, with magnetic nanoparticles in a conductive metal matrix, are expected to have unusual mechanical, electrical and magnetic properties.

SESSION F2: NANOPHASE CERAMICS
Chair: Horst Hahn and Richard W. Siegel
Monday Afternoon, November 29, 1999
Salon F (M)

1:30 PM F2.1
SYNTHESIS AND CHARACTERIZATION OF NANO-CRYSTALLINE CERAMICS. Markus Winterer, Thin Films Division, Materials Science Department, Darmstadt University of Technology, Darmstadt, GERMANY.

Nanocrystalline materials are characterized by a large fraction of atoms located in interfaces, i.e. surfaces or grain boundaries. This particular microstructure is the source for heterogeneous disorder and novel properties of these materials. The influence of synthesis methods and parameters on the structure of nanocrystalline zirconia will be presented. EXAFS spectroscopy provides structure information independent of the degree of disorder. Partial pair distribution functions can be extracted by Reverse Monte Carlo Modelling. This is supplemented by complementary methods, XRD, NDP, SEM and TEM. This will provide a consistent picture on crystallinity, crystallographic structure and distribution of defects in these materials. Structure and microstructure of nanocrystalline ceramics are correlated to the synthesis procedures.

2:00 PM F2.2
THE SYNTHESIS OF NANO-CRYSTALLINE CERAMICS BY A NOVEL ELECTROSTATIC SPRAY ASSISTED VAPOR DEPOSITION METHOD. Kwangs-Leong Choy, Imperial College of Science, Technology & Medicine, Department of Materials, London, UNITED KINGDOM.

This contribution presents an overview of an emerging cost-effective Electrostatic Spray Assisted Vapor Deposition (ESAD) process for the synthesis of nanocrystalline oxide and non-oxide ceramics. This process involves spraying atomised charged precursor droplets across an electric field in an open atmosphere to initiate either homogeneous or heterogeneous chemical reactions for the synthesis of either continuous solid films or powder particles. The composition of the material can be controlled by tailoring the chemistry of the precursors. This anionic deposition method can operate at low processing temperatures and provide high purity materials with structural control at the nanometer scale level. The versatility of ESAD has led to the deposition of films and powders for a wide range of applications, including electrical, optoelectronic, magnetic, structural and functional applications. A comparison between the ESAD and other conventional vapour processing techniques such as Physical Vapour Deposition and Chemical Vapour Deposition will be made. The application of ESAD to the production of nanocrystalline ceramics will be reviewed and the benefits of ESAD will be addressed. The scientific and technological significance of the ESAD method will be presented. The fundamental aspects of ESAD including process principle, deposition mechanism, reaction chemistry, thermodynamics/kinetics, and transport phenomena of chemical precursors will be presented. The experimental set up of ESAD and the influence of various process parameters (e.g. deposition temperature, field strength and particle flow rate, deposition time etc) on the structure and properties of the materials will be reviewed. The paper will also include the recent development work of ESAD technologies based on different heating and aerosol generation methods. The technical viability of this process to be scaled up for large area and large scale production of nanocrystalline films and powder particles will be addressed.
2:30 PM P2.3
UNUSUAL PREPARATION OF NANOPHASIC MATERIALS
BASED ON TETRANYLIC OXIDE. Georges Denes, Arnaud Guene, Eva
Lucas, Stephane Le Huerou, Abdelbakaia Misset, and Frederic
Nicolas, Concordia University, Dept of Chemistry and Biochemistry,
Laboratory of Solid State Chemistry and Moosahur Spectroscopy
and Laboratories for Inorganic Materials, Montreal, Quebec, CANADA.

Nanophase tetralenic oxide SnO₂ is usually prepared by rapid
hydrolysis of Sn(IV) alk or an organometal(IV). Sn(IV) oxide is a
well-known material with numerous applications. In this work, we
identified and studied a novel method for preparing nanocrystalline
SnO₂, and in some cases nanocomposites containing SnO₂ and Sn(II)
and/or other tin(IV) species. The novelty of the method lies in the fact
that it is performed using a diamond tile, namely tin(II) fluorde SnF₂,
upon oxidation with a limited amount of hydrogen peroxide. The material obtained consists of nanoparticles of SnO₂ nH₂O
(\~n = 2), which can be easily dehydrated at moderately high
temperature without the need to form a nanocrystalline particle
growth and recrystallization to rutile type SnO₂ is obtained upon
heating at higher temperature, to give microcrystalline. Depending on
the SnO₂/SnF₂ ratio in the reaction mixture, nanocomposites of
SnO₂ containing divalent and/or tetravalent tin oxide/titania are
obtained. The preparation and results will be presented.

2:45 PM P2.4
A NOVEL METHOD FOR SINTERING NANOPHASIC CERAMICS
WITHOUT GRAIN GROWTH. Le Wei Chen, University of
Pennsylvania, Department of Materials Science and Engineering,
Philadelphia, PA.

While very fine powders may initially have a better sinterability,
particle coarsening and grain growth usually prevail to prevent
obtaining fine grain sizes in the fully dense bodies. Indeed, according
to the size of the grain established during sintering, grain growth is inevitable during final stage sintering, defined as the stage
when the density exceeds 90%. To circumvent this problem, high
pressure has often been used to promote densification without
grain growth. We show here a novel two-step pressureless sintering method
which allows complete densification without any grain growth. As
a result, fully dense yttrium oxide bodies with a grain size of 60 nm
have been obtained. The processing window and the kinetics of
growthless sintering suggest important mechanisms that differentiate
grain boundary diffusion and grain boundary migration. Evidence for
a threshold process for grain boundary diffusion is also manifest. This
method has not been applied to a number of oxides resulting in
nanostructured materials.

3:30 PM P2.5
PREPARATION METHODS AND SUPERPLASTIC PROPERTIES
OF FINE-GRAINED SILICA OR ALUMINA DOPED
TETRAEDRAL ZIRCONIA. Yoshihiko Saito, Thoru S. Suzuki,
Tetsuo Uchikoshi, Keiji Mori and Koji Hirohisa, National Research
Institute for Metals, Tsukuba, JAPAN.

Preliminary studies of fine-grained yttria doped tetragonal zirconia
(Y-T/Z) and its composites have shown that certain requirements must
be met to achieve superplastic fine grain size. Homogeneous microstructure and the inhibition of grain growth during
high-temperature deformation. These requirements are being met both
through advances in powder preparation and through novel development in sintering and processing, such as colloidal processing.
Particle dispersion control is the most important factor in colloidal
processing. The dispersion of particles in aqueous suspensions can be
stabilized by electrostatic repulsion or electrostatic repulsion. Stabilizes
of tetragonal zirconia, silica-zirconia, and alumina-zirconia fine
particles were prepared by adjusting the pH value or adding
appropriate amounts of polyelectrolyte. These bodies were obtained through colloidal filtration, followed by cold “miscroscopic”
pressing (CTP). Temperatures exceeding 1000°C can be obtained for Alumina doped Y-T/Z/Y-T/Z with a grain size of 300 nm was successfully prepared by sintering
chemically synthesized powder. To obtain a dense Y-T/Z with a grain
diameter less than 100 nm, however, a special procedure is necessary. We
processed fine-grained (1) monoclinic zirconia polycrystals using a
monolithic zirconia-sol prepared by wet processing, and (2)
CoO-doped Y-T/Z using a Co-absorbed Y-T/Z suspension, where both
suspensions were directly consolidated by pressure filtration without a
dry powder pressing.

4:00 PM P2.6
PREPARATION AND CHARACTERIZATION OF LARGE AREA
NANOCRYSTALLINE TiO₂ FILMS FOR SOLID STATE SOLAR
CELLS. Krishna C. Mandal, Bryce K. Dille, David Ruser, EIC
Laboratories, Inc., Norwood, MA; O. Swaidgo, Materials Engineering
Department, Ecole Polytechnique, Montréal, CANADA.

This paper describes a novel large area nanocrystalline titanium
dioxide (TiO₂) film used in fabricating high efficiency photoelectrochemical (PEC) solar cells. The prepared films are highly
reproducible and were thoroughly characterized by XRD, EDX, AFM,
and XPS methods. These films have been synthesized using a
Ru-bipyridyl based dye, and passivated using either tert-butyl
pyridine or ammonia. The sensitized and passivated films are then
used in fabricating La-biased solar cells, which the devices demonstrated open-circuit voltages ( Voc) of ~0.86V,
short-circuit current densities ( Jsc) of 13.2 mA/cm², fill factors of
0.7, and conversion efficiencies of 8.62%. The fabrication steps,
directed toward large production volumes, included a quality
controlled fabrication procedure developed at EIC Laboratories, Inc.
The results presented in this paper show the highest achieved
efficiency obtained so far for a polymer-based nanocrystalline TiO₂
solar cell.

4:15 PM P2.7
THE PROCESSING OF NANOSTRUCTURED ZIRCONIUM
OXIDE-BASED MATERIALS FOR SOLID ACID CATALYSIS.
Michael S. Weng and Jackie Y. Ying, Massachusetts Institute of
Technology, Dept of Chemical Engineering, Cambridge, MA.

Zirconium oxide-based materials have garnered much interest as solid
catalysts, due to the unusual surface acidity properties of
zirconium oxide. The acidic strength and type of acid site of zirconia
can be manipulated by adding metallic species to the surface or by
combining with a second metal oxide in the bulk. Accordingly, a
variety of zirconium oxide-based acid materials have been synthesized in
such manner. As the conventional preparation methods involve only
the control of (bulk and surface) composition of these materials, relatively little importance has been placed on the effect of
microstructure on surface acidity and acid catalytic activity. Through
novel wet chemical techniques, nanostructured zirconia-based
composites can be prepared, and the catalytic properties of these
acidic materials can be observed. Nanostructured zirconia-based acid
materials were synthesized through several different methods.
Surface-terminated processing led to highly porous zirconia acidic
composites, such as zirconia-silica and zirconia-alumina, where the mesopores contain tremendous internal surface areas. The pore sizes could
be tailored in the range of 2-10 nm by adjusting the length of the
surface-terminated molecule and by using auxiliary organics.

Hydrothermal processing of sulfated zirconia composites led to
nanostructured zirconia materials that demonstrated enhanced resistance to
desorption from coking, the major problem limiting industrial use of
solid acid catalysts. Grain size and crystal phase could be controlled
with hydrothermal treatment temperature and with the use of yttria
as a second oxide. The preparation of other zirconia composites
involved the mutual dispersion of zirconia and the second oxide.
Targeted for acidic catalytic applications, these different types of
zirconia materials represent the successful progress in nanostructured
techniques through many processing techniques.

4:30 PM P2.8
CONTINUOUS WAVE LASER ACTION FROM LANTHANIDE
DOPED NANOALUMINA POWDERS, SYNTHESIS AND
PROPERTIES. R.M. Line, T. Hinklin, S. Rand, and G. Williams,
Dept of Materials Science and Engineering, Chemistry and the
Applied Physics Division, University of Michigan, Ann Arbor, MI.

Nano-sized alumina powders doped with lanthanides can be produced
by flame spray pyrolysis (FSP) of very similar, low cost aluminum
precursors doped with oxides. This scalable synthesis route produces
single crystal nanomaterials at ~ 100 g/h with surface areas of 50-120
m²/g. Typical powders consist of homogeneously doped single
particles, with particle sizes ranging from 10-30 nm average diameter. Similar microstructures can be obtained for other
alloys that form a solid solution. By reducing the size of the particles
and thus the interparticle cavity, the scattering regime is changed from
diffuse to strong scattering causing photon localization. Light
emission is due to the localization within the grain medium. Details
concerning the alkoxide chemistry, flame spray pyrolysis, and the
lasing behavior of nanoized doped powders will be discussed.

4:45 PM P2.9
HIGH SURFACE AREA CERAMIC POWDERS WITH MINIMAL
AGGREGATION. Gurleen Saini, Amit Singh, Nanopowder
Enterprises Inc., Piscataway, NJ; Nick Glamme, Bernard H. Kerr,
Rutgers-The State University of New Jersey, Piscataway, NJ.

For many applications, it is essential to have high surface area
ceramic powders that have a narrow particle size distribution and a
minimum amount of aggregation. We have addressed the challenge
to produce such nanoparticles at high production rates and in
9:30 AM F3.4

PROTON CONDUCTING ORGANIC/INORGANIC NANOCOMPOSITES POLYMER ELECTROLYTE MEMBRANE THROUGH SOL-GEL PROCESSES. Itaru Honna, H. Nakajima.

High temperature protonic conducting polymer membrane provides new technological applications in the electrochemical devices including electrochromic displays, chemical sensors, fuel cells and others. Organic/inorganic nanocomposites membrane consists of SiO₂/PTMO (Polymer of tetramethylene oxide) hybrid are remarkable family of isotropic, flexible, amorphous polymer materials, which has been synthesized through solgel processes. The hybrid membrane doped with acid can serve as membrane for acid mixture such as monodecylphosphoric acid or phosphotungstic acid shows good protonic conductivities at high temperatures above 100°C. The protonic conductive membrane was found to be thermally stable at high temperatures because of the inorganic SiO₂ framework within the nanocomposites matrix. In this paper, the organic/inorganic nanocomposite membrane consists of SiO₂ / PEO as well as SiO₂/PTMO hybrids has been synthesized through solgel processes. The composite membrane can be derived by hydrolysis and condensation reaction of polymer precursors consists of polyethylene oxides endcapped with trihydroxylamine and monophenyl-trihydroxyamine (Mph). The process is same for PTMO derivatives. The membrane was found to be composed of nanophase composites between inorganics and organics at nm scale. The membrane doped with acid molecules such as monodecylphosphoric acid (MDP) or phosphotungstic acid (PWA) shows good protonic conductivities around 0.1 - 1.0 mS/cm at temperatures up to 160°C and was found to be a flexible as well as thermally stable ion conducting polymer electrolyte for high temperature electrochemical devices.

9:45 AM F3.5

PREPARATION OF AEROGEL AND XEROGEL NANOCOMPOSITES MATERIALS. Maria Francesca Cauzia, Anna Corrias, Giorgio Paschini, Ca’fèrari Univ. Dept of Chemical Science, Cagliari, ITALY.

Nanocomposite materials composed of nanometric metric or metal oxides particles embedded in aerogel matrices, possess a variety of interesting magnetic, electric and catalytic properties, that are strongly size-dependent. Nanocomposites can be prepared by several techniques such as impregnation, deposition methods and ball milling techniques. The solgel process has been used for the preparation of nanocomposite materials. The process is affected by several parameters which allow a versatile control of the structural, morphological and chemical properties of these materials. In this paper we present the results of the solgel preparation of silica oxide-silica and iron oxide-silica nanocomposite materials using TEOS and either nickel nitrate or iron nitrate as precursors. In order to obtain aerogels with a high surface area and pore volumes the drying step of the aerogels is performed under supercritical conditions with xerogel, in which the original pore structure of the aerogels is lost, they are obtained by slowly removing the solvent. The effects of different drying procedures on the structural and morphological properties of aerogels were followed by X-ray diffractometry, and atomic force microscopy. The formation of precursors in different morphologies of silica particles as a function of processing conditions will be discussed, and the mechanism of crystalline silica formation on functionalized organic templates will be suggested based on experimental results.

10:30 AM F3.6

CERAMIC NANOCOMPOSITES AS NEW BUILDING BLOCKS FOR MEMS. Alfredo M. Morales, Marcelo Gonzales and Jill M. Hruby, Sandia National Laboratories, Livermore, CA.

Many revolutionary devices and processes in the macroscopic world involve ceramics and composites. In contrast, very few ceramic materials are available for the fabrication of microelecromechanical systems (MEMS). The incorporation of ceramics into microscale devices would allow the exploitation of novel properties such as increased strength, high temperature inerterness, chemical and biological compatibility, magnetism, piezoelectricity, and photochromism. In this talk, we will present recent results on the use of ceramic nanocomposites in the fabrication of MEMS microcomponents. Our fabrication technique consists of 1) formulation of a nanocomposite mixture; 2) micromolding; 3) curing and photoinitiation; 4) chemical removal of the mold. Micromolded components can be produced free standing or assembled on substrates. By using particles with nanometer diameters, we are able to mold components with lateral dimensions in the order of a few...
Molecular weight control in a polymer monolayer formed by a surface initiated polymerization. Dale L. Huber and Thomas A. P. Seery, University of Connecticut, Polymer Program, Storrs, CT.

A model nanocomposite consisting of gold nanoparticles coalesced with a monolayer of poly (hexyl isocyanate) has been prepared through a polymerization reaction initiated at the surfaces of the particles. This polymerization has been studied in real time by infrared spectroscopy to determine the growth rate of the reaction and utilized to prepare nanocomposites with carefully tailored molecular dimension. Dynamic light scattering in conjunction with transmission electron microscopy have been used to characterize the sizes of the resultant nanocomposites, and the measured sizes have been related to scaling predictions for tethered polymers. The polymeric constituent of the prepared nanocomposites has been thoroughly characterized to determine the molecular weight and polydispersity of the surface bound polymer. The properties of the polymer formed at surfaces were then compared to polymers formed through analogous solution polymerizations.

Surface metallized composite polyimide films via in situ reduction of silver(I) beta-diketone complexes. Paul Scalise, Robin E. Southward, National Research Council, Langley Research Center, NASA, Hampton, VA; David W. Thompson, Department of Chemistry, The College of William and Mary, Williamsburg, VA.

The fabrication of optical mirrors with polymeric rather than glass supports can reduce weight and fragility. Silver is a metal of choice for a reflecting surface. Here we report that thermal curing of a silver(I) beta-diketone containing polymeric acid from 3,3'-4,4'diphenyltetrahydroxyxillic acid, BTDA, and 4,4'-dicyanodimide, ODA, in dimethylacetamide leads both to polyimide films via cyclodehydration and to reduction of silver(I) to give nanometer-sized metal particles dispersed throughout the bulk of the film. During the cure a portion of the silver aggregates at the surface to give surfaces that have excellent reflecting properties. Adhesion of the surface silver to polyimide is superb via a mechanical interlocking mechanism. The resulting metallized composite films retain mechanical and thermal properties similar to the parent polyimide. X-ray diffraction shows crystalline silver in the films after thermal curing. Silver remains in the bulk of the polyimide film with varying particle sizes of ca. 15-20 nm. The interior of the metallized films is not electrically conducting. Films were characterized by X-ray, DSC, TGA, XPS, TEM, and SEM.


The semiconducting group-III nitrides show great promise for electronic and optoelectronic devices. In the case of Gallium Nitride there are some unique properties like a wide and direct bandgap of 3.45 eV, low compressibility, high thermal conductivity, chemical inertness and high dielectric constant. While the formation of thin films of GaN realized by MOCVD or MBE has been well established leading to quantum wells currently used in devices (bright blue LEDs and laser diodes), there is no satisfying chemical process available to produce quantum-confined GaN structures in less than two dimensions. Conventional lithographic or etching techniques are rather costly and connected with limited resolution. Besides there is excitonic quenching at etched/damaged boundaries. The mesoporous molecular sieve MCM-41, due to its combinatorial arrangement of uniform pores (10-20 nm in diameter) of hollow cylinders offers a possibility for synthesizing mesoscopic composites by inclusion chemistry. If homogeneously filled with GaN, a GaN@MCM-41 composite would result in an ordered array of uniform quantum dots in the molecular sieve matrix. We describe the organization of nanodispersed GaN in MCM-41 of 2.7 nm pore diameter via impregnation with a solution of the single-source precursor trimethylsilyl-gallium in toluene. The XRD observations showing the expected type-I system of MCM-41 still being intact after the loading with Gallium Nitride (GaN content about 1.0 wt.-%, molar ratio GaN : N = 0.7 to 1). The decrease of the BET surface area of the composites, GaN/MCM-41 of about 10% in comparison of that of pure MCM-41 material give a strong hint for porefilling, which is emphasized by the overall reduced intensity of the low-angle XRD pattern of the composites. In addition optical investigations (photoluminescence and excitation spectroscopy) showed a blue-shifted bandgap of about 3.7 eV indicate nanodispersed Gallium Nitride to be present inside the pores of MCM-41.

Preparation of a homogeneously dispersed barium titanate/polymer nanocomposite thin films. David E. Gills, Elliott B. Shumowich, School of Materials Engineering, Purdue University, West Lafayette, IN.

Crystalline nanoparticles of barium titanate (BITO) dispersed in a polymer matrix were processed by reacting block copolymer films loaded with titanium dioxide/bis(ethylenecarbonate) (TIE) in aqueous solutions of barium hydroxide at 80°C. Using a poly(styrene-b-polbutadiene triblock copolymer (SB) as the polymer matrix resulted in segregated polymer-rich or BITO-rich regions in the film. In contrast, a homogenous dispersion of BITO particles was achieved by using poly(styrene-co-maleic anhydride) as the polymer matrix. For TIE concentrations in large mole excess of the maleic anhydride, BITO nanoparticles were observed throughout the polymer matrix. However, BITO was absent from the film at lower TIE concentrations. Fourier transform infrared spectroscopy suggests that the TIE altered the maleic anhydride functionality. The results resulted in an increased miscibility between the TIE and the polymer, thereby facilitating BITO dispersion.

Nanophase fiber coatings by electrophoretic deposition for ceramic matrix composites. Theodore M. Breslau, John J. Henry, Jr., Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN.

Control of the mechanical properties of the fiber-matrix interface in ceramic fiber-ceramic matrix composites is critical for obtaining desired composite properties. Typically, adhesion between the fiber and matrix must be sufficiently weak to allow crack deflection around the fibers. This is generally accomplished with a fiber coating that either adjusts the adhesion between fiber and matrix or is itself sufficiently weak to provide a crack pathway. This paper reports the initial development of a new class of fiber-coating systems from electrophoretically deposited, nanoscale, silicon-carbide powder for silicon carbide-matrix, silicon carbide-based fiber systems. Research sponsored by the U. S. Department of Energy, Office of Fossil Energy, Advanced Research and Technology Development Materials Program, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation.

SESSION F4: NANOPHASE SEMICONDUCTORS
Chair: John C. Parker
Tuesday Afternoon, November 30, 1999
Salon F (M)
1:30 PM F4.1
Nano-crystal engineering: 3-D self-assembly of semiconductor nanowires. Geoffrey F. Strouse, University of California at Santa Barbara, Santa Barbara, CA.

The assembly of semiconductor components into flexible, 3-dimensional arrays opens new routes into the design and preparation of nano-scale electronic materials. Efforts in metal chalcogenide at the 100 nm scale have opened new routes into materials that exhibit quantized physical properties, with the capacity for selective surface coupling. These materials can be synthesized as nearly nano-disperse with controlled surface coupling via hydrothermal methods. Selective coupling of the composites with energy and electron transfer appendages allow analysis of carrier transport in 3D architectures. We have developed novel approaches for the selective substitution and assembly of a series of nano-scale metallo-sulfur-, -tellurium semiconductors that are readily modified at both the metal-chalcogenide core and surface coupling, making these materials ideal for crystal-engineering approaches to nano-electronics. We will discuss the unique advantage of using metal-cluster precursors for nano-assembly and the application of bio-inspired self-assembly for the preparation of a 3-dimensional architectures. Applications of 3-D engineering for electron transport will be probed. Correlation of the optical properties and mass spectrometry will be discussed.

1:45 PM F4.2
All-inorganic field effect transistors fabricated by PRINTING. Brent A. Hiltz, Babak Nivi, Joseph M. Jacobson.
Massachusetts Institute of Technology, Medin Lab, Cambridge, MA.

We have developed a novel nanocrystal preparation that yields a monodisperse 1.7 nm CdTe nanocrystal solution without intimately bound organic capping groups. This solution is used to print the semiconductor in an inorganic thin-film transistor (TFT) with field effect mobility exceeding the best available. The printed film assembles into single crystalline domains consisting of tens of nanocrystals. To the best of our knowledge, these devices represent the first all-inorganic transistors with a printed inorganic semiconductor and represent the highest mobility printed TFTs to date. This process suggests a new, all-printed, method of fabricating high-performance inorganic logic.

2:00 PM P4.3 SYNTHESIS OF UNAGGLOMERATED, NON-OXIDE NANOPHASE POWDERS IN A TURBULENT JET FLAME Lee J. Rosen, Richard L. Aulburn, Washington Univ., Dept. of Mechanical Engineering, St. Louis, MO.

Of the many different methods used to produce nanoparticle powders, few are able to achieve fabrication rates while minimizing the agglomeration of particles. Furthermore, the powders produced, if non-oxide, must be handled using costly techniques due to their highly reactive nature. Recently, a flame synthesis process conceptually similar to commercial flame processes used to produce millions of tons of ceramic and carbon black powder annually, was extended to allow the production of unagglomerated, non-oxide nanoparticle powders. This technique employs an encapsulation step during the thermal-oxidation stage to control particle size, prevent agglomeration and protect the powders from oxidation/hydration during post-synthesis handling. The encapsulation material (typically a salt) can be removed during post-flame processing. A Monte Carlo numerical simulation suggests that the encapsulation process occurs in two steps. Initially the flame-synthesized particles grow normally, but upon condensation of the encapsulation material (salt) the size distribution transitions into a bimodal size distribution, with the coarse mode consisting primarily of salt. The coarse mode then acts to scavenge the fine mode. The final morphology of the core particles will depend upon the scavenging process and behavior of the core particles within the scavenging particles. Numerical results suggest that the size distribution of the core particles within the scavenging particles can be much narrower than that of a single-component self-preserving aerosol. The sodium/halide flame and encapsulation process has been used to produce a variety of metals and ceramics (e.g., Ti, W, AI, TiB2, Al2O3) of various sizes (ca. 2-50 nm) using a laminar jet flame. Recently, the laminar facility has been converted to a turbulent jet facility to demonstrate the scalability of the process. Experimental results will be presented for the synthesis of metal powder in the turbulent jet facility showing the influence of various process parameters on encapsulation efficiency as well as particle morphology.

2:15 PM P4.4 SYNTHESIS AND CHARACTERIZATION OF STRONGLY FLUORESCENT CdTe NANOCRYSTAL COLLOIDS. Frederic V. Mitkev, Mengi G. Bissendri, Massachusetts Institute of Technology, Dept. of Chemistry, Cambridge, MA.

We present a synthesis of colloidal CdTe nanocrystals whose absolute room temperature quantum yields are routinely above 60%. The preparation is the traditional top-down (TD) method reported by Murray, with a more stable tellurium precursor now used as the chalcogenide source. The photoluminescence is continuously tunable over the range 500-760 nm and is as narrow as 135 nm (45 nm FWHM). No deep trap luminescence is detected for the diameter range 4-11 nm. CdTe nanocrystals are characterized by transmission electron microscopy and powder X-ray diffraction. Examinations are proposed to help us understand CdTe nanocrystals that are more highly dispersed than those presently characterized using the top-down method.

2:30 PM P4.5 LOCAL ORDERING OF SEMICONDUCTOR SINGLE CRYSTALS FOLLOWING NONLINEAR EXCITATION OF LATTICE ATOMS. P. Sen, School of Physical Sciences, Jawaharlal Nehru University, New Delhi, India; J. Akhtar, Semiconductor Devices Area, CERI, Pilani, INDIA.

Organization of atoms in the nanometer-scale lattice can have both electronic and optical properties. Low energy ion implantation and irradiation effects take place on a local length scale compared to the size of the system under illumination, and has been extensively employed for modifying bulk electrical as well as mechanical properties. But, it lacks the ability to control small regions with unique properties that has failed to yield results, due to the formation of complex defects and defect clusters which interfere with any desirable atomic arrangement. With the advent of MeV ions, a new scenario has emerged with the possibility of nonlinear energy transfer from the incident lattice to the electrons, first to the lattice and then to the electron lattice through phonon coupling[1]. Further, these ions travel considerable distance (several microns) inside a solid, slowing down while transferring its energy, making it possible to produce bulk modifications. In this presentation we demonstrate that this novel energy transfer mechanism is capable of modifying an already ordered lattice into small locally recrystallized phases producing atomically sharp interfaces. Employing scanning tunneling microscopy (STM) we study these interfaces and determine their electronic properties. The arrangements alter the local electronic density of state (DOS) which is reflected in the adsorption/packeting property of these surfaces, shown here as a time-elapsed water adsorption experiment.


2:45 PM P4.6 SYNTHESIS OF SILICON NANOPARTICLES BY CO2 LASER PYROLYSIS METHOD AND GROWTH OF HIGHLY TEXTURED DIAMOND FILMS ON Si (100) SUBSTRATES BY NANO- PARTICLE SEEDING TECHNIQUE. Anishk Kumar, Sabina Betti, M. Galve, MA George. Department of Electrical and Computer Engineering, University of South Alabama, Mobile, AL, 1. ENEA, Dipartimento Innovazione, Divisione Fisica Applicata, Centro Ricerche Framatome, Rome, ITALY. 2. Center for Materials and Surface Science, The University of Alabama in Huntsville, AL.

Nanostructures powders, with particle size in the 1-10 nm range, have shown great promise in the formation of advanced structural and functional materials for applications in tribological coatings, high surface area catalysis support for photoelectrochemical cells, electronic and optical coatings, capacitor and battery materials, dielectric and optoelectronic materials. CO2 laser synthesis of ceramic powders from gas-phase precursors is an ideal method for growing nanosized, pure and nearly monodispersed particles. The silicon nanoparticles have been grown by CO2 laser induced pyrolysis of silane in gas flow reactor. The Si nanoparticles have been characterized using SEM, TEM, XRD and XPS techniques. We report a novel approach of seeding Si nanoparticles on Si(100) substrates, which has resulted high quality smooth diamond films deposited by HFCVD method. The seeding technique has increased the adhesion of diamond films and helps to grow high quality textured diamond films. The detailed investigations to grow high quality diamond films will be discussed in this paper.

3:00 PM P4.7 OPTICAL EFFECTS OF SURFACE MODIFICATION OF SEMICONDUCTOR NANOPARTICLES USING CHALCOGEN SITES. Tong Ni, Dattatrey Nagesha, Nicholas Kotev, Oklahoma State University, Chemistry Department, Stillwater, OK.

Chemical binding to metal atoms located on the surface of II-VI semiconductor nanoparticles, NP, is widely used for their surface modification including the derivatization with various organic moieties. Conversely, interfacial chalcogen atoms have not been utilized for binding of organic ligands to NP. Among the properties that differ them from the metal sites, the most important one is the fact that the surface chalcogen atoms are electronically conjugated to the second state of NP. This feature warrants the consideration of chalcogen modification as tool for controlling optical and electronic properties of nanoparticles. The attachment of organic groups with delocalized p-systems to chalcogen atoms was achieved by reaction with cyclodextrin biopyridine complexes of copper, ruthenium, platinum and palladium. The structure of the complexes was confirmed by NMR, ESR, TEM, XRD and ES-SAXED dyn. UV-VIS absorption, emission, and excitation spectra suggest relaxation of the electron confinement effect and partial mixing of electronic states of the semiconductor core and p-systems of the aromatic ligands. Quantum mechanical calculations demonstrate the formation of electron states connecting the nanoparticle core and the delocalized p-system of biopyridine ligand, which is supported by the observation of efficient electronic coupling between the semiconductor core and the modifier. The transition of excitation energy was observed for the excitonic emission of the semiconductor core as well as for the surface trap emission. Chalcogen modification was demonstrated to be applicable to various size-quantized semiconductor colloids - CdS, CdTe and newly synthesized strongly luminescing Bi2Se3.

3:45 PM P4.8 FORMATION OF NANOCRYSTALLINE SiC POWDER FROM CHLORINE-CONTAINING POLYCARBONATE PRECURSORS. Brian R. Mitchell, Hung Yung, B. F. Goodrich Chemical Co. University, Dean of Chemical Engineering, New Orleans, LA; Martin Ade, Dirk Kurentbach, Eberhard Müller, TU Bergakademie Freiberg, Institute für Keramische Werksstoffe, Freiberg, GERMANY.

Nanocrystalline β-SiC particles with a grain size range of 5-20 nm were prepared by heating a pre-pyrolyzed, chlorine-containing
polyethylene/polyacrylamide (PS/PCPs) to 1000° C. The transformation from the pre-polymerized PS/PCPs to nanocrystalline SiC was investigated by thermal analysis (TG), X-ray diffraction (XRD), mass-spectrometry and infrared spectroscopy. The results indicated that the nanocrystalline SiC was formed by the crystallization of the PS/PCPs without any support, and crosslinking of Si-Si, Si-C, and Si-CH$_2$-Si bonds. The TEM observation showed that SiC particles consist of equixed, randomly oriented, ultrafine grains.

4:40 PM F4.9

STRUCTURE OF POLYCRYSTALLINE SILICON FILMS BY GLOW-DISCHARGE DECOMPOSITION USING SiH$_4$/SiF$_4$ AT LOW TEMPERATURES during the presentation from Jun'ichi Nakao, Yoshihisa Kurata, Shizuo Hisemura, Department of Electronics, Faculty of Technology, Kansai University, Kansai, JAPAN.

Polycrystalline silicon (pol-Si) films were prepared on a silicon substrate at 300°C by a plasma-enhanced chemical vapor deposition method using a mixture of gases SiH$_4$/SiF$_4$ with two different H$_2$ flow rates ($H_2 = 0$ or 10 sccm) as a function of RF power. Effects caused by the addition and without addition of H$_2$ on the structural properties of the films were investigated by means of Raman scattering, X-ray diffraction (XRD), Electron spin resonance (ESR), Fourier-Transform infrared spectroscopy (FT-IR), and AFM measurements. The pol-Si films deposited under the both deposition conditions had shown <110> preferential orientation and the deposition rate were in the range of 2.920 nm/min. For $H_2 = 0$ sccm, both the grain size $d$ and the crystalline volume fraction $\phi$ increased first and then decreased, having the maximum value at around 120 nm, 80% respectively, as the RF power increased. On the other hand, for $H_2 = 10$ sccm, both $d$ and $\phi$ values were deteriorated as the RF power increased having the maximum value around 10 nm and 70% respectively. It was suggested that the deterioration of the crystalline quality with the addition of hydrogen, is likely to be caused by the suppression of the role of R-related radicals along with the effect of a change in the surface morphology of the substrate as well as the effect of in situ chemical etching on the growing surface. Probable, mechanisms causing the change in the crystalline quality are also discussed.

4:15 PM F4.10

SYNTHESIS OF CdSe/CdS CORE/SHIELD NANOCRYSTALS FROM STABLE SINGLE MOLECULE PRECURSORS. M. Amez & N. Monika, Paul O'Brien and Neeraj K. Verghese, Department of Chemistry, Imperial College of Science, Technology and Medicine, Exhibition Road, London, UK.

TOPO (tris(n-octylphosphine oxide) capped CdSe/CdS, CdSe/ZnS, and CdSe/ZnSe core/shell nanocrystals have been synthesized from the thermolysis of bis[methyl(n-hexyl)di(thiolencarbamato)]cadmium(II) and bis[methyl(n-hexyl)di(thiolencarbamato)]cadmium/Zn(II), as precursors. The nanoparticles obtained show a red shift in the absorption spectrum with an enhanced photoluminescence. The Selected Area Electron Diffraction (SAED), X-ray diffraction (XRD) pattern, and Transmission Electron Microscopy (TEM) show the material to be predominantly of the hexagonal phase. Energy dispersive analysis by X-ray (EDAX) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) show the presence of Cd, Se, and S. The properties of these structures will be compared against the ternary and quaternary phases (CdZnS, CdZnSe, and CdZnSeS), which are being synthesized.

4:30 PM F4.11

ELECTROCHEMICAL ATOMIC LAYER EPITAXY, ELECTRODEPOSITION OF III-V AND II-VI SEMICONDUCTOR COMPOUNDS. Travis L. Wed, Billy H. Flowers Jr., John L. Stickney, Univ. of Georgia, Dept. of Chemistry, Athens, Georgia, GA; Uwe Hegge, University of Georgia, Dept. of Physics, Athens, GA.

Thin films of InAs and CdTe have been electrodeposited by electrochemical atomic layer epitaxy (electrochemical ALE). The deposition procedure forms films of a new atomic layer at a time. This atomic layer deposition takes advantage of surface limited reactions referred to as under potential deposition (UPD). UPD occurs when it is energetically more favorable for one element to deposit another element than for it to deposit on itself, due to the energy of compound formation. Once the substrate is coated with an atomic layer of an element, the deposition will stop. Next a second element is introduced, resulting in a layer of the compound. This sequence is repeated to form a thin film of desired thickness using a flow cell with automated solution delivery. The sequence is termed electrochemical ALE.

4:45 PM F4.12

TAYLORED SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF CHALCOGENIDE NANOCRYSTALS FROM LANGMUIR-BLODGETT TEMPLES. L. Cristofolini, M.P. Festus, Dipartimento di Fisica, Universita' di Perugia, ITALY; F. Facci, Dipartimento di Scienze Ambientali, Universita' de Tuscia, Viterbo, ITALY.

We synthesized IL-VI chalcogenide nanocrystals (size 1 to 4 nm) of mixed composition grown in fatty acid Langmuir-Blogett multilayer templates. The controlled production of homogeneous chalcogenide nanocrystals Cd$_2$S$_2$, ZnSe, and II-VI compounds in addition to the synthesis was the characterization of the chemical composition for the fine tuning of the electronic properties of semiconductor nanocrystals and in particular the band gap. The samples thus produced are characterized by quasi-resonance micro-Raman and spectroscopy.

SESSION F5 - POSTER SESSION: NANOCOMPOSITES - SYNTHESIS, CHARACTERIZATION, AND PROPERTIES

Chairs: Horst Hahn, Srini Ramamurthy and John C. Parker

Tuesday November 30, 1999

8:00 PM

Exhibition Hall B (H)

F5.1 MICROSTRUCTURAL AND ELECTRICAL CHARACTERIZATION OF SOL-GEL DERIVED Pb(Zr,Ti)$_x$O$_{3}$ NANOCOMPOSITE CERAMICS AND THIN FILMS. Ming Dong, Zuo C. Ye, Department of Chemistry, Simon Fraser University, Burnaby, BC, CANADA.

Ferrocene PbZr$_{1-x}$Ti$_x$O$_3$ nano-powders were synthesized by an air-stable sol-gel route. These fine powders allow us to study high and high density PZT ceramics at temperatures lower than 1000°C. The specimens strain about 9% of the theoretical density. PZT nanocomposites ceramics and thin films were prepared from high purity sol-gel dried PZT powder and small amount (0.1-1.0 vol%) of solgel derived MoO$_3$. The microstructure of the nanocomposites were investigated by XRD and SEM. The piezoelectric and ferroelectric properties were measured using an RT66A Standard Ferroelectric Test System and an MTI-2000 Foton. The frequency and temperature dependence of the dielectric properties of these ceramics were determined by impedance spectroscopy from room temperature to 500°C at frequencies ranging from 1 to 10$^6$ Hz, using a Solartron 1260 Impedance analyzer combined with a Solartron 1296 Dielectric Interface. The pure PZT ceramics show a Curie temperature of 400°C with a significant frequency dispersion of the dielectric constant observed at C, which was attributed to the highly conductive grain boundary effects. At room temperature, the dielectric constant k and the dissipation factor k are 850 and 0.025, respectively. The temperature dependence of both k and d by dc conductivity indicate an activation energy of 1.10 eV. The bulk conductivity of the pure PZT ceramics is about 10$^{-13}$ Sm$^{-1}$ at 40°C. Effects of the oxide additives on the electric microstructure, the grain size and grain boundary, the ac and dc conductivity, and the dielectric and piezoelectric properties of the PZT-related nanocomposites were discussed based on the experimental results.

F5.2 OPTICAL CHARACTERIZATION OF PMMA-CARBON NANTOTUBE NANOCOMPOSITES. E. Gregory, D.J. Tarbox, R. Cesar, Dept. of Physics and Astronomy, Clemson University, Clemson SC; J. Ballato, Dept. of Ceramic and Materials Engineering, Clemson University, Clemson SC; P. M. Ajayin, Dept. Material Science and Engineering, Rensselaer Polytechnic Institute, Troy; NY; D. L. Carroll, Dept. Physics and Astronomy, Clemson University, Clemson SC.

Optical phenomena in composites of poly(methylmethacrylate) (PMMA) and purified carbon nanotubes have been quantified as a function of nanotube concentration (multiwalled vs. single walled), doping, and dispersion. The optical response of multiwalled nanotubes (MWNts) well dispersed in a PMMA matrix shows scattering to be dominate from the Near-UV to the Near-IR. However, single walled nanotube dispersions show several absorption features in the UV-Vis and FTIR spectra. This work coupled with TEM observations suggests that SWNT-PMMA and MWNT-PMMA interactions differ dramatically. The effect of these differences will be discussed in terms of the resulting optical, electronic, and thermal properties of the composite.

F5.3 NANOTUBE-POLYMER COMPOSITES: MECHANICAL AND
ELECTRICAL PROPERTIES. Boucha Safari, Rodney Andrews, Frank Derbyshire, Center for Applied Energy Research, University of Kentucky, Lexington, KY.

The inclusion of multiwalled carbon nanotubes (MWNTs) in polymer matrices greatly enhances the physical properties and electrical conductivity of the resulting composites. MWNTs were dispersed in matrices of polystyrene (PS) or polyurethane (PF) resin at concentrations of up to 7.5 wt%. The tensile strength, elastic modulus, strain to failure and electrical conductivity of the resulting composites were measured for various MWNT loadings. Uniform dispersion of the MWNTs into the matrix proved to be a critical factor, with optimal property enhancement achieved by dispersion in which the nanotubes were separated and dispersed. PS films were transformed from an insulating to a conductive material, with conductivities approaching 1 cm²/cm². The properties of the PPF-MWNT composites were similarly increased. This increase in composite conductivity increased with increasing MWNT loading and decreased with increasing concentration of MWNTs. The PS films approximately double both the tensile strength and the stiffness at about 5% MWNT loading. While blank PS samples fail plastically, the MWNT-PS composites show little plastic deformation on failure, indicating a stiffening of the composite with nanotube inclusion. In contrast, for the brittle PPF matrix, improvements to the polymer flexibility (160% reduction in flexural modulus) were observed. It is tentatively concluded that the properties of the MWNTs dominate those of the matrix in determining the composite material behavior.

F5.4 PHASE TRANSITION AND CONTROL OF SELF-ASSEMBLED MESOSTRUCTURED VANADIA/SURFACTANT COMPOSITES. Ibrahah Hamma, Y. Yagi, H.S. Zhou, A. Endo, M. Miyawaki, T. Kudo.

Mesosporous materials invented by scientists of the Mobil Corporation have attracted considerable interest for application in electronics, energy, and environmental device materials. In this work, we have synthesized mesoporous vanadia/surfactant composite in powder as well as thin film form and characterized its mesostructure and electrochemical properties. The mesoporous Vanadate materials were formed by surfactant templated mechanism similar to MCM silica synthesis and phase transition mechanism of Alcl₃, boric acid, and silicon. The vanadene mesostructure was synthesized as follows; the ammoniumvanadate (NH₄VO₃) 1.0 g, was first dissolved in a aqueous solution (18g) with an amount of addition of NaOH (1.3g) to be converted completely at pH 7. The CV (10μA) (0.15μA) is dissolved in the above solution with no precipitation at this pH, HCl (0.1N) added drop wise to gradually decrease solution’s pH to around 1. As HCl adding, passing neutral point, vanadium start precipitating at the surface of the micelle and mesostructured vanadium were formed. Also, similarly, the mesostructure of vanadium/surfactant thin films were synthesized on the substrate by spin coating technique. The solution was prepared by hydrolyzed sol of Vanadium potassium precursor. The XRD patterns show a smaller structure to a larger one, the size of the mesopores decreased from 5.8 nm to 2.4 nm upon thermal treatment, which indicates the mesopores of LC extremely important in the determination of the properties of the materials. We used mesostructured materials, both with hydrophilic and hydrophobic surfaces, filling mesoporous liquid crystals. The results of this study will be presented in detail at the conference.

F5.5 NANOCOMPOSITES MATERIAL LIQUID CRYSTAL-AEROSIL PARTICLES: DIELECTRIC AND PHOTON CORRELATION SPECTROSCOPY INVESTIGATIONS. P.M. Aliev and G.P. Sinha, Department of Physics, University of Puerto Rico, San Juan, PR.

Nematic liquid crystal (LC) filled with aerosil particles – prospective inorganic-organic nanocomposite material for optoelectronic application – have been investigated by broadband dielectric spectroscopy (BDS), static light scattering and photon correlation spectroscopy. The aerosil particles with sizes of 10 nm in diameter in filled nematic liquid crystals form a network structure with linear size of LC domains about 250 nm with random distribution of the director orientation of each domain. This material has very developed liquid crystal phase and provides a base for the development of the unique LC properties of LC extremely important in the determination of the properties of the material. We used particles, both with hydrophilic and hydrophobic surfaces, filling nematic liquid crystal 5CB. PCS probes dynamics of gold and silver nanoparticles embedded inside nematic LC, while BDS provides information on reorientational motion of polar molecules of liquid crystal. We found that the properties of 5CB are considerably affected by the network. Two bulk-like modes due to the rotation of mesogens and the tumbling motion of LC molecules were found to be modified in filled 5CB. Additionally, a low frequency relaxation process and dispersion of dielectric permittivity due to conductivity were also observed. The treatment of the surface of filling particles has strongest influence on the properties of the slow process and least important for molecular modes. The characteristic frequencies of the slow process are lower for hydrophilic particles and in this sample the contribution of this process to the total polarization was greater than in the case of hydrophobic particles. Preliminary experiment shows that two new relaxation processes appear in filled 5CB in addition to the director fluctuation process in bulk. This work is supported by DoD grant N00014-04-1-0558.

F5.6 MECHANICAL PROPERTIES OF NANOPARTICLE FILLED POLYMERS. L.S. Schaller, R.W. Siegel, C.B. Ng, B.J. Ash, Rensselaer Polytechnic Institute, Materials Science and Engineering Department, Troy, NY.

The tensile, scratch, and impact properties of nanocomposites made from either epoxy or polyethylene/maleic anhydride (PMMA) filled with titania nanoparticles were investigated as a function of nanoparticle size, loading, dispersion, and filler-matrix interaction. The filler was dispersed using sonication, and we found that there is a narrow viscosity window in which fillers with relatively poor filler/matrix interaction can be dispersed. In addition, we characterized the change in epoxy resin chemical structure as a result of the sonication using infrared and solid state nuclear magnetic resonance spectroscopies. In the epoxy based nanocomposites, we observed a simultaneous increase in modulus and strain-to-failure, and a dramatic improvement in the scratch resistance compared to epoxy composites containing micron sized titanium particles. The dispersion of the nanoparticles was crucial in determining the increase in strain-to-failure. The addition of this modifier decreased the glass transition temperature by 7°C at 20% loading. Similar behavior was observed in filled PMMA samples. The latest results from this ongoing project will be reported.

This work was supported by the National Science Foundation.


Pillared clays now attract a great deal of attention as catalysts of various industrially important processes including those of environmental catalysis such as NO₂ selective reduction by ammonia and for hydrocarbons. This work will present results of design and studies of systems based upon alumina- and zirconia-pillared montmorillonite. To modify pillared adsorption properties and thermal stability, lanthanum and alkaline-earth cations were introduced into polycrystals. Clusters of copper and cobalt cations were fixed at pillared using ion-exchange and polymeric methods, and nanocrystals of Pt, Pd and Ag were then inserted into galleries using impregnation or photo-assisted deposition. For comparison, model nanocomposites comprised of copper and cobalt cations clusters with suspended precious metals clusters supported on high quality alumina and zirconia partially stabilized by Cr, Sr, Ba and La were also synthesized. Pore structure of samples was characterized using detailed analysis of nitrogen adsorption isotherms and XRD. Bulk structure, microstructure and spatial distribution of separate components studied by TEM, XRD, SAXS and EXAFS were compared with the surface properties of nanocomposites characterized by EELS spectroscopy of hydroxyls and adsorbed test molecules (CO, NO, N₂O). TPR. Spectra of pillared structure are compared with that of bulk dispersed aluminia and zirconia phases was elucidated, and its effects on interaction between oxidic and metallic particles was elucidated. Nanocomposites performance in the reaction of NO selective reduction by Cu-C10 hydrocarbons in the excess of oxygen was shown to be enhanced due to co-action of oxidic and metallic components. FTIR in situ was applied to detect surface reaction intermediates (nitro-nitrates, nitrates etc) and estimate their reactions. All these data were used to discuss catalytic properties of nanocomposites based upon pillared clays. This work is supported by INTAS under INTAS 97-11729 project.

F5.8 NEW PREPARATIVE METHODS FOR ORGANIC-INORGANIC POLYMER HYBRIDS. Ryo Tanaka, Yashiki Chaju, Kyoto Univ., Dept. of Polymer Chemistry, Kyoto, JAPAN.

This paper describes new methods for the preparation of...
Replacing the current on-chip insulator (silicon dioxide, dielectric constant of approximately 4.0) with low dielectric constant materials can greatly improve the performance of high density VLSI devices by reducing cross-talk and capacitive coupling between metal interconnects. Polytetrafluoroethylene (PTFE) has the lowest dielectric constant (κ < 2.0) of any full density material, which makes it a promising candidate for IC applications. Pure PTFE thin films cast from PTFE-nanocomposite containing sub-20nm PTFE particles, though thermally stable, has some inherent sub-optimal properties including adhesion strength to other inorganic materials and mechanical strength at high processing temperatures. In order to improve these properties, we have developed a PTFE/silicon compound nanocomposite material. Initial tests have shown that this nanocomposite material rival with conventional high temperature mechanical properties and interfacial properties between the composite and inorganic materials such as silicon, silicone oxide, silicon nitride and some metals. The surface roughness of the thin film coatings is also reduced compared to pure PTFE thin film coatings. Characterization has been carried out using different techniques such as DMA, FTIR, XPS depth profiling, SMS, NR, SANS and AFM with selective etching, in order to understand this novel nanocomposite and its surface and interfacial properties.

F5.12
A NOVEL LIQUID PHASE PROCESSING ROUTE TO CONTROL GRAIN GROWTH IN NANOPHASE AND NANOCOMPOSITE ALUMINA COMPACTS. Deborah M. Vernon, James C. Truman, Elizabeth K. Reilly and Janet Rankin, Brown University, Division of Engineering, Providence, RI.

A novel processing route to produce nanophas and nanocomposite materials is being investigated. Pellets of submicron and nanoscale starting powder are pressed to >50% theoretical density. Processing involves an introduction of an initial powder pressing and sintering. During the intermediate step, a second phase precursor is introduced into the pore structure via liquid phase infiltration. The infiltrated porous pellets are subsequently heated to elevated temperatures between 1200 and 1650 °C for a range of times, to produce a fully dense final microstructure. The effects of varying initial pellet densities, infiltrant concentrations, infiltrant species and final sintering schedules have been studied. Final microstructures were characterized using a variety of techniques. Grain growth and depth of infiltration were measured using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). High resolution electron microscopy (HREM) and electron energy loss spectroscopy (EELS) were used to study the grain boundaries in the infiltrated pellets. Microhardness measurements were also performed. For most cases studied here, the introduction of a second phase via liquid infiltration produced a microstructure with significantly reduced grain growth, and improved hardness measurements when compared to control samples.

F5.13
MICROSTRUCTURAL INVESTIGATION OF MONOLITHIC ZrB2 AND ZrB2-ZrC COMPOSITES. Kyuyoung Kim, Seon Woo Lee, Kwang Bo Shin, Hanyang University, Ceramic Processing Research Center, Dept of Ceramic Engineering, Seoul, KOREA.

The addition of rare-earth elements (La and Nd) to pure boride (ZrB2) and ZrB2-ZrC composite was considered to improve their sinterabilities during pressureless sintering. And other solidification methods such as GPS and SPS were also employed to control the convention pressureless sintering method. In case of composite three different batches compositions were selected near the eutectic point of ZrB2-ZrC. It was found that the additives improved remarkably the sinterability but their effective parameters were different from two additives in both two bodies. Transmission electron microscopy was performed to analyze their aspects in micro-scale.

F5.14
PERIODIC METAL AND CARBON NANOFIBERS FOR THERMOELECTRICITY AND THERMO-ELECTROCHEMICAL POWER GENERATION. Dyna I. Khvostikin, Mikhail E. Kozlov, New Jersey Institute of Technology, Newark, NJ; Igor Udos, L.M. Liu, Anurav A. Zakhidov, Roy H. Bruggeman, Allied Signal, Inc., Morristown, NJ; Geoff M. Sankins, University of Wollongong, Wollongong, AUSTRALIA.

Three-dimensionally periodic metal and carbon nanofibers have been fabricated that are the inverse of the precursor silica opals used as molds. In the two-step preparation, either molten bismuth, antimony and their alloys were infiltrated into the opal under high pressure or carbon was infiltrated into the opal by both the CVD technique and the precursor pyrolysis route. At the second step, silica was chemically removed by hydrofluoric acid to leave a periodic mesh of the metal and carbon tetrahedron carbides through narrow interconnects. For thermoelectrics, we anticipated that
scattering processes at the interconnects and the highly extended internal surface might improve performance by having a greater effect on photon-modified (hotspot) thermal conductivity than on electrical conductivity. As expected, the thermal conductivity reduction is much larger for vacuum-filled nanocomposites than for the unetched thermoelectric-silica nanocomposite. Also, the electrical conductivity of the thermoelectric nanocomposites shows semiconducting-type behavior (in contrast to the metallic type behavior of the bulk thermoelectric), which can be described by weak 3D localization in a mesoscopic system. For power generation, the carbon nanofibers (having great interest in surface modification) were tested in AlOx in carbon nanotube/thermoelectric converters (TCs) that can convert waste heat to electrical energy. Maintaining the temperature gradient of only about 60°C between the two ends of the as-prepared 30% [HNO3]/aqueous electrolyte, we obtain an open circuit voltage of 70 mV and a short-circuit electric current of 3.6 mA per gram of electrode material. The values obtained are comparable to those provided by more expensive carbon nanotubes and nanofibers electrodes. Various electronic devices can be produced to improve the characteristics of the carbon nanofiber TC. *Supported by DARPA grants DAAH-09-7-C-036 and N00173-99-0000.

**F.5.15 SYNTHESIS AND MECHANICAL PROPERTIES OF TiC/n-C:H NANOCONPONENTS WITH SURFACE COATING**

W. J. Meng. Department of Mechanical Engineering, Louisiana State University, Baton Rouge, LA; P.M. Baldes, L.E. Rehn, Materials Science Division, Argonne National Laboratory, Argonne, IL.

We report the use of a conventional reactive sputtering system and a low-pressure high-density plasma based hybrid physical vapor deposition (PVD)/chemical vapor deposition (CVD) system for the synthesis of tantalum-containing hydrocarbon (TiC/n-C:H) thin surface coatings with a variable nickel Ti composition. We show that all TiC/n-C:H coatings are titanium carbide/amorphous hydrocarbons (TiC/n-C:H) thin film nanocomposites. We show further that the elastic modulus (E) and hardness (H) of reaction sputter deposited TiC/n-C:H nanocomposites approach to those of nanomechanical bounds on E and H for two-phase composites. We observe in addition that E and H of TiC/n-C:H made by hybrid PVD/CVD exhibit large apparent deviations from the nanomechanical bounds. We probe the hydrogen concentration in TiC/n-C:H nanocomposites experimentally and discuss the role of hydrogen in determining the mechanical properties of TiC/n-C:H nanocomposites.


Ion implantation and thermal processing were used to create NiS nanocrystals in SiO2 and Al2O3 hosts. NiS and Ni are particularly interesting because they span a wide range of compositions and structural properties with different electronic properties. Pure stoichiometric NiS is hexagonal [Nascent structure] at room temperature. Bulk heating at room temperature by rapid cooling, under 90°C, metal-semiconductor transition at ~100°C. If cooled slowly below 380°C, it spontaneously transforms to the metallic face-centered cubic form. Nanocrystalline NiS also occurs in two phases with different characteristics: NiS and NiS2. In the present work, we study the formation of nanocrystals precipitates containing NiS and Ni, formed by ion implantation into SiO2 and Al2O3 hosts. The optical data are compared to those obtained for a reference sample implanted with Ni only. When formed in SiO2, the resulting samples have a composition close to NiS, as measured by energy dispersive X-ray spectroscopy. The microstructure, size, and crystallinity of the nanocrystals was characterized by transmission electron microscopy, and the experimental transmission data showed a sharp absorption peak at 450 nm that did not occur for the sample implanted with nickel only. Initial data suggest that this may be the surface plasmon for metallic NiS. The peak becomes more pronounced at higher annealing temperatures. In Al2O3, both the optical and the X-ray diffraction data imply the presence of more than one NiS phase and the strong absorption at 450 nm was considerably weaker than for an SO2 host. An additional broad absorption peak occurred at 342 nm in Al2O3 samples missed above 800°C. The presence of a potential metal semiconductor transition was investigated by performing the absorption measurements at cryogenic temperatures. The results suggest that there is no sharp transition between the metallic and semiconductor.

**F.5.17 ULTRAHIGH NANOCONPONENTS TITANIIUM NITRIDE/TITANIIUM SILICIDE WITH HARDNESS EXCEEDING 100 GPa AND HIGH FRACTURE TOUGHNESS. Stan Veprek, Andreas Niederhofer, Kolin Moto, Pavel Neshale, T. Bolkan and Hans Meinhold, Institute for Chemistry of Inorganic Materials, Technical University Munich, Garching, Munich, GERMANY.**

In course of a further development of our concept for the design of superhard nanocomposite materials, we succeeded to prepare coatings consisting of nanostructured titanic nitride and titanium silicide which reach vickers microhardness of more than 100 GPa independent of the applied load between 30 and 100 mN. The absence of any radial cracks at a load of a high fraction of these coatings which also show a high elastic recovery approaching 90%. The elastic modulus and the universal hardness (hardness under load) compares well with diamond which was measured for comparison. The coatings of a thickness of up to 11 microns were prepared by means of plasma CVD at 560°C. We shall present the results of the hardness measurements to underline their reliability. In the second part of the presentation we shall report experimental data and discuss the thermodynamics of the formation of the three-phase nanocomposites with increasing content of silicon in the coatings. The data strongly supports the view that these nanocomposites are thermodynamically stabilized.

**F.5.18 CRACK HEALING IN ALUMINA/SILICON CARBIDE NANOCOMPOSITES AFTER GRINDING AND ANNEALING. H.C. Wu, J. T. Nishimura, S.G. Roberts, Department of Materials, University of Oxford, Oxford, UK, B. Derby, Manchester Structural Science Centre, UMIST, Manchester, UK.**

Alumina/silicon carbide nanocomposites are known to show their highest strength levels after surface grinding followed by annealing. The strength of bend specimens with smoothly ground nanocomposite surfaces exceeds that of specimens with a well-polished surface after annealing in flowing Ar. The bend strength of the ground surface also shows some small improvement on annealing. TEM investigations of annealed cross-sections show that the annealing treatments lead to surface crack healing. The chemical composition of the healed cracks has been studied by high resolution FE-STEM and the likely chemical reactions will be discussed.

**F.5.19 PHASE EVOLUTION IN SPUTTER DEPOSITED ZIRCONIA/TITANIUM NANOULARITE FILMS. J.D. DeLong and C.R. Ardi, University of Wisconsin-Milwaukee, Department of Electrical Engineering and Computer Science, Department of Materials, and the Laboratory for Surface Studies, Milwaukee, WI.**

The films in this study consist of multiple bilayer stacks containing zinc oxide and titania laminated together on the nanometer scale by the reactive sputter deposition process. We previously used a ceramic nanolaminate structure for phase control in zirconia/alumina and zirconia–yttria nanolaminates grown at room temperature. In zirconia–yttria–alumina nanolaminates, the compositions retained their chemical identity, and there was no interfacial reaction. In contrast, an interfacial reaction in zirconia–yttria–alumina nanolaminates completely obliterated yttria as a separate entity. Work on zirconia–yttria–alumina nanolaminates demonstrated that when the interfaces could be controlled, the nucleation form at low temperature in a system in which the bulk equilibrium phase diagram predicts reaction between components. The zirconia–yttria–alumina system provides a middle ground in reactive interfacial chemistry with the extremes provided by nanolaminates of zirconia and very reactive zirconia–yttria. The goal of the present paper is to correlate bilayer architecture with phase evolution and interface structure in zirconia–yttria–alumina nanolaminates films grown on room temperature silicon substrates by sequential reactive sputter deposition from zirconium and titania elemental targets. Nanolaminates with seventeen different bilayer architectures were studied. Diffraction and ultraviolet-visible spectrophotometry techniques were used for film characterization. The results show that an interface occurred between zirconia and titania layers. Phase evolution in the zirconia layers in nanolaminates with ultrathin (1.5 nm) titania layers was dependent upon this interfacial reaction. Specifically, < 100 > orientation, high refractive index cubic zirconia was stabilized in zirconia layers between 16 and 22 nm. This crystal orientation indicates that cubic zirconia growth is ordered by the lowest energy planes of the simple cubic unit cell of the fluorite structure. Increasing the zirconia layer thickness beyond 22 nm in nanolaminates with ultrathin titania layers resulted in zirconia recrystallization and the formation of other zirconia phases. Increasing the titania layer thickness quenched the formation of < 100 > cubic zirconia resulting in a variscite structure.

**F.5.20 COATING OF SILICON CARBIDE ON SILICON NANOYIRES BY DIRECT LOW-ENERGY ION BEAM DEPOSITION. Hongxing Peng, X.T. Zhou, N. Wang, S.T. Lee, City University of
Hong Kong, Dept of Physics and Materials Science, Hong Kong, CHINA.

The successful bulk-scale synthesis of Si nanowires by laser ablation or thermal evaporation has aroused great interest in this one-dimensional material. The field emission current of silicon emitters widely used for flat panel display devices was found to increase significantly by a thin SiC coating through a chemical conversion process. In present study, silicon nanowires with diameters around 20 nm were subjected to methane, argon and hydrogen ion bombardment at 997 K for 10 hours with an ion current density of 1.5 μA/cm². TEM observations showed that the product remained to be nanowires with diameter ranging from 20 nm to 40 nm. The corresponding electron diffraction pattern revealed that both Si and Si-C nanowires were present. Dark field TEM images showed that the silicon diffraction ring comes from the core of the nanowires, while the silicon carbide ring comes from the outer layers of the nanowires. Detailed observations at high magnification identified that a thin silicon carbide polycrystal was grown uniformly on the silicon carbide surface. The thickness of the SiC outer layer was found to be as thin as 3-4 nm. Most of the SiC nanoparticles were found to be oriented and separated with a Si core by a thin layer of Silicon. The Raman peak of the composite nanowires was about 20 cm⁻¹ lower than that of the silicon nanowires. The photoluminescence intensity of the nanowires after cooling with SiC became stronger and sharper, and the peak blueshift appeared much larger.

F5.21
OPTICAL RESPONSE OF COMPOSITE Al₂O₃ FILMS WITH Cu INSERTED NANO-CRYSTALS PRODUCED BY PULSED LASER DEPOSITION M. Garcia de la Roque, J. Solis, Instituto de Optica, CSIC, Madrid, SPAIN. P. Smit, F. Thiery, Universiteit Gent, Kassel, Kassel, GERMANY.

Thin films formed by metal nanocrystals embedded in insulating matrices, usually oxides, are being intensively investigated for the development of compact integrated ultrafast optical switches. Thus synthesis methods compatible with the growth of good quality oxides and the development of metal nanocrystals are required. Pulsed laser deposition has demonstrated to have high potential both for oxide deposition and for the development of artificial structures.

In this paper we aim to show a systematic study of the optical linear and nonlinear properties of the superlattice nanostructured Cu-Al₂O₃ film embedded in an amorphous Al₂O₃ matrix, in which a good control of the average size of the metal nanocrystals and its in-depth distribution is achieved. The Cu-Al₂O₃ thin films are produced by alternate ablation of independent targets, in a controlled gas environment. Nanostructured films have been obtained with characteristic nanocrystal Cu sizes varying from 2 nm to 8 nm, and with Cu-Cu nanocrystal in-depth separations changing from 5 nm to 20 nm. The optical absorption spectra of the films show the characteristic enhancement close to the expected surface plasmon resonance wavelength for Cu nanocrystals. The changes in the linear and nonlinear optical properties will be discussed as function of the Cu nanocrystal size, morphology, in-depth separation, in addition to the possible reactions at the metal to nanocrystal interface.

F5.22
THE FORMATION OF HIGH-COERCIVITY, ORIENTED NANOPHASE MAGNETIC PRECIPITATES IN OXIDE SINGLE CRYSTALS BY ION IMPLANTATION. Miki Hori, Frank A. Modine, Tony E. Hughes, Aktivnias M. Idjin, John D. Budai, Kenjiro Sensui, Thomas H. Geballe, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN.

Ion implantation and thermal processing methods have been used to form nanophase ferromagnetic or superparamagnetic precipitates that are embedded in the near-surface region of single crystals of Al₂O₃ and yttrium-stabilized (cubic) zirconia (YSZ). Specifically, ferromagnetic precipitates have been produced by the ion implantation of Co, Ni, and Fe, and either metal or oxide precipitates may be formed depending on the properties of the annealing atmosphere. In general, the precipitates are faceted, isolated single-crystal precipitates. The precipitates are roughly oriented with respect to the host Al₂O₃ or YSZ lattice. In the Co case, embedded nanophase precipitates were formed by the implantation of Co⁺ at an energy of 100 kV and a dose of 8 x 10¹⁵ ions/cm² followed by annealing in a reducing atmosphere. The implanted/amended Co depth profile, the particle size distributions and shapes, and the orientational relationships between the ferromagnetic nanophase precipitates and the host crystal lattice were determined using RBS/channeling, TEM, and X-ray diffraction. The magnetic coercivity effects arising from the ferromagnetic precipitates formed in the Al₂O₃ and YSZ host were observed and characterized using magnetic circular dichroism. The details of the magnetic properties of the implanted/amended Al₂O₃ and YSZ host were characterized using magnetic circular dichroism. The details of the magnetic properties of the implanted/amended Al₂O₃ and YSZ host were characterized using magnetic circular dichroism. The details of the magnetic properties of the implanted/amended Al₂O₃ and YSZ host were characterized using magnetic circular dichroism.

F5.20
XPS STUDY OF Pt/Ce1-xZrO2/Si COMPOSITE SYSTEMS.
R. Sporken, A. Galtrywski, Univ. of Namur, Laboratoire LISE, Namur, BELGIUM, K. Keyeney, MPijol, Ecole des Mines, Saint-Etienne, FRANCE, R. Baker and S. Bernal, Universidad de Cadiz, Cadiz, SPAIN.

Cerium oxide is widely used as a promoter in three-way catalysts for exhaust systems in gasoline burning car engines. Adding ZrO2 to CeO2 significantly improves its thermal stability and its ability to store and release oxygen under reaction conditions. To study the interaction between noble metals and the mixed oxide on a model system, we have prepared Pt/Ce1-xZrO2/Si (111) composite systems and studied them with x-ray photoelectron spectroscopy and x-ray diffraction. Thin films of Ce1-xZrO2 mixed oxides (about 10-30 nm thick) were grown on Si(111) substrates by electron beam evaporation. The composition of the films was determined by XPS and EDX and found to be slightly enriched in Ce compared to the source material. XPS depth profiles showed the following structure, starting from the substrate: a region of interdiffused Zr and Si, a CeSiO4 layer mixed with ZrO2 and finally a homogeneous Ce1-xZrO2 film. X-ray diffraction confirmed the presence of CeO2 mixed oxide and suggests the presence of ZrO2 and CeO2 in some of the samples. Pt was evaporated onto these mixed oxide films. The deposition of Pt was interrupted several times to record XPS spectra. Eventually, the Pt/Ce/FeO5 system was submitted to reducing and oxidizing conditions to study the effect of the noble metal - support interaction. It was found that, in contrast to noble metal - oxide powder composite systems, the noble metal always stays in the oxidized state even after the Pt is oxidized by higher binding energy. The low Pt coverage can be explained by a cluster size effect, where screening of the core hole created by the photoemission is less efficient for very small clusters.

F5.27
PHOTOVOLTAIC DEVICES FROM POLYMERIC-NANOPARTICLE COMPOSITES.

Photovoltaic devices based on composites with polythiophene with silicon and titanium nanoclusters have been fabricated. The device efficiency was measured as a function of the nanoparticle concentration, the thickness of the composite layer and for various electrode materials. The optical and electrical properties of the composites were studied in order to enhance the device performance. The electrical properties were correlated with the morphology of the composites. The influence of organic modification of the nanoparticles on the device performance was also investigated.

F5.28
MICROSTRUCTURAL EVALUATION OF PRECURSOR DERIVED SiC:O BULK CERAMICS.
Kenichi Kikukawa, Fumihiko Watanabe, Japan Science and Technology Corporation, Nagoya, JAPAN; Isao Hiroshi Bill, Fritz Aldinger, Max-Planck-Institut für Metall Forschung, Stuttgart, GERMANY.

We have recently fabricated SiC:O bulk ceramics with a variety of non-equilibrium compositions by pyrolysis of silicon polymeric (PCS) body with given amounts of oxygen. The oxygen introduction within PCS molecular structure made the body insoluble during the pyrolysis stage and sustained its burning as well as an increase of the ceramic yield. The Si:C atomic ratio of the ceramics was easily controllable and much higher than that of conventional SiC:O glasses ceramics which are derived from silicon alkoxide precursors including some tetramethyldiamine carbon units. Therefore, this procedure is also expected to be suitable for preparation of SiC:SiO2 nanocomposites by in-situ carbothermic reduction reaction at high temperature. The present paper specifically reports the microstructure of the various SiC:O glasses ceramics and describes the effect of different processing conditions on the microstructure. The ceramic body after pyrolysis to 1550K showed fine microstructure of SiC nano grains with amorphous phase. The grain diameter, the porosity of the body decreased with increasing oxygen content. The specimen with a higher packing density also demonstrated both of a smaller SiC grain size and a finer pore size. This microstructure particularly contained a large number of free-carbon phases which is believed to have been caused by the self internal reactive gasification of pyrolytic methane and hydrogen gases. Such a carbon phase was useful to inhibit rapid SiC grain growth. A SiC/SiO2 nanocomposite which was prepared at 1870K kept fine microstructure with SiC grain size of 40nm or maximum. The relationship between processing atmosphere and surface bulk composition is also discussed in this paper.

F5.29
MICRO-RAMAN STUDY OF SELF-ASSEMBLED NANO-STRUCTURES: 1-xP2ZnN-xP7 SOLID SOLUTION. S. Gupta, R.S. Koyan, Department of Physics, Univ. of Puerto Rico, San Juan, PR; A. Bihain, Materials Research Laboratory, Pennsylvania State University, University Park, PA.

Refractive ferroelectrics are one of the important classes of self-assembled nanostructure composite materials. Interesting features associated with the nanoregions give rise to the most interesting device related characteristics and unusual properties in these materials. Besides, they possess the largest property coefficients alone and when modified with lead titanate (PT) as well. In this report, a detailed study has been carried out on 1-xP2ZnN-xP7 refractors with compositions x = 0.05 and 0.15 by polarized Raman scattering under various optical and E-field variables and inferred the structure-property relations in order to obtain enough information to extract the material for matching the application criteria. In addition, phase transitions associated with the rare earths have also been investigated to understand the polarization mechanism(s) for unpoled and poled specimen. Authors wish to acknowledge the following NSF-DMR-991729 and DAAH56-98-1-0012 grants for financial support.

F5.30
ROOM TEMPERATURE LUMINESCENCE FROM ULTRATHIN Si/SiO2 MULTILAYERS PREPARED BY RF CO-SPUTTERING.
M. Burznanu, O. Resto, L.P. Rasscan, and S.Z. Weisz, Department of Physics, University of Puerto Rico, San Juan, PR.

Multilayered structures of Si and SiO2 films with thicknesses ranging from 40nm to 2mm were deposited by using sequential RF sputtering. The depth of penetration of the layered structures were characterized by Auger spectroscopy and TEM microscopy. The crystallinity was studied by electron diffraction technique. We discuss the dependence of the room temperature photoluminescence on the thickness of the films and the number of layers. Other optical properties as optical absorption were also obtained to get information about the energy gap size of the silicon films. We discuss the dependence of the optical properties of the multilayers on the structural parameters and we compare our results with photoluminescent nanocrystallines Si/SiO2 samples grown with the same technique.

F5.31
STUDY OF THE LUMINESCENCE OF Eu-DOPED NANOCRYSTALLINE Si/SiO2 SYSTEMS PREPARED BY RF CO-SPUTTERING.
N. Gery, L.P. Rasscan, O. Resto, and S.Z. Weisz, Department of Physics, University of Puerto Rico, San Juan, PR; A. Mihulac and H. Liu, Department of Physics, University of Puerto Rico, Mayaguez, PR.

Eu-doped nanocrystalline silicon structures were prepared by RF co-sputtering. The host material is silicon particles with sizes ranging from 1-3nm to 2-3nm embedded in SiO2. The optical properties of the undoped and doped materials were characterized using piceinosecond and CW laser sources. We found that the luminescence due to Eu-doping is strongly dependent on the synthesis conditions. We correlated the optical properties with the nanoparticle size distributions and the valence state of the dopant. We offer conclusions about the dependence of the Eu-photoluminescence on the Eu-impurities on the intensity on the energy gap sizes of the semiconductor nanocrystals.

F5.32
TITANIUM DIOXIDE AND APATITE COATED POROUS CERAMICS PHOTOCATALYSTS.
Tori Nonomi, Shinji Kono, Hiroshi Taoda, National Industrial Research Institute of Nagoya, Dept of Multi Functional Materials, Nagoya, JAPAN; Tomoyuki Ohno, Kansai, JAPAN.

Titanium dioxide can photo-oxidize organic chemical materials in water and air; when it is illuminated. Apatite is useful in absorption of bacteria, viruses etc. If apatite and titanium dioxide can been combined into a composite with the attributes of both, this composite may be a good antibacterial and environmental purification material, having the ability to absorb and to decompose bacteria and other organic materials. Titanium dioxide was coated on the surface of the porous ceramics by sol-gel method, then the ceramics was soaked in a
pseudo body solution containing excess phosphate ions. After soaking in the pseudo body solution for 1 day, a bone-like apatite layer was formed on the surface of the titanium disc. This ceramic has resolved various organisms such as methylene blue. The apatite-coated titanium disc film could be used for antibacterial and environmental purification.

F5.33
SYNTHESIS OF LOW-DIMENSIONAL NANOSTRUCTURES USING LAYERED DOUBLE HYDROXIDES AS NANOFACTORS
Alexey V. Vertegel, Y. Kalinin, M. V. K. Kalinin, P. Nikiforov, Yuri D. Troyakov, Higher School of Materials Science, Moscow State University, Moscow, RUSSIA.

A novel method for the preparation of nanostructured materials is discussed. The method is based on the chemical modification of anion-substituted layered double hydroxides (LDH). It combines the simplicity of chemical methods and a possibility of preparation of two, one-, or zero-dimensional nanostructures of the following metal-micelle matrices. LDHs have a general formula \( \text{M}_2 \text{M}_2 \text{(OH)}_2 \) [anion] \(-/+-/\text{H}_2\text{O}\), where M\(_1\) and M\(_2\) are metals in the oxidation state +2 and +3, respectively, and anion \(-/-\) is virtually any anion, which does not form a stable complex with M\(_1\) or M\(_2\). A structure of an LDH consists of positively charged hydroxide layers \([\text{M}_2 \text{M}_2 \text{(OH)}_2]^{2+}\) bonded with negatively charged anions, which occupy the interlayer space. Due to the relatively large interlayer distance, the anions in LDHs are relatively easy to exchange and it is possible to obtain species with practically stoichiometric content of an appropriate anion \(-/-\.

In the present paper, we use the reduction of LDHs containing EDTA complexes of Fe(III), Ni(II) and Cu(II) in the interlayer space for the preparation of nanostructured nanocomposites of the corresponding metals. Also, thermal decomposition of an LDH substituted with \(\text{Pb}_2\text{(S}_2\text{O}_3)_2\)\(^{2+}\) anions has been used for the preparation of PbS nanoparticles. When reduction or decomposition of an anion \(-/-\) occurs, hydroxide layers of LDH restrict the reaction area. Thus, the interlayer anion controls the one-dimensional nanostructure resulting in the formation of low-dimensional nanostructures.

F5.34
STOICHIOMETRY CONTROL IN MOLECULAR BEAM DEPOSITED NANOCRYSTALLINE SnO\(_2\) AND TiO\(_2\) THIN FILMS.
Holger Hohe, Horst Hahn, Felix Eidelberg, Ralf Nagel, Stefan Flege, Adam Baligh, Technical University of Darmstadt, Dept. of Materials Sciences, GERMANY.

Molecular beam deposition (MB) of thin film metal oxide is prospective for application in gas sensor technology due to the high space control over thickness and composition. However, the MB process leads to some oxygen deficiency in the oxide. Further application of the MB technology (and, in general, the e-beam deposition in vacuum) for growing nanostructures needs the control and correction of the oxygen stoichiometry by adding in-situ atomic oxygen to the growing material or via the thin film oxidation after deposition. Thin films (about 50nm) of SnO\(_2\) and TiO\(_2\) were deposited on on silicon substrates at 1100°C by MB from SnO\(_2\) and TiO\(_2\) sources. The film stoichiometry in the as-deposited state is characterized by XRD, RBS and SIMS. The films were annealed in oxygen at various temperatures and time to characterize changes in the film stoichiometry and kinetics of O\(_2\) reaction with SnO\(_2\) and TiO\(_2\). The grain size evolution in films during O\(_2\)-annealing was controlled by TEM. The results show the influence of oxygen content in the SnO\(_2\) and TiO\(_2\) thin films for different oxygen pressures in the MB setup will be presented. In conclusion, we discuss a problem, whether this system makes possible to eliminate the high-temperature postdeposition stage of the oxygen stoichiometry correction in the oxide.

F5.35
BLOCK AND STAR COPOlyMERIC NANO-COMPOSITES.
H Chen, R.P. Ginnelis, Cornell Univ., Dept. of Materials Science and Engineering, Ithaca, NY; M.W. Weimer, O.A. Scherman, D. Sgts, D. Cornell Univ., Dept. of Chemistry and Chemical Biological; M. Pitsikalis, N. Hadjiipatridis, Univ. of Athens, Dept. of Chemistry, Athens, GREECE.

Polymer-silicate nanocomposites have generated great interest among researchers, mainly because of their much more improved properties comparing with pure polymers and their conventional composites. They also provide an ideal model to investigate the structure and dynamics of polymer in nanocomposites. However, most of the work to date has focused on homopolymers. Here we present work on nanocomposites made of block and star copolymer and organically modified silicates. The mobility of confined copolymers both under and above their respective order-disorder transition temperatures, as well as the effect of the existence of silicate nanorod on the microphase transition of the copolymer will be discussed.

F5.36
SOFT ZnWO\(_4\) ON HARD W N SELF-LUBRICATION NANO-COMPOSITE COATINGS.
M. Vedavyas, D. Patel, G. Watsukewa and Ashok Kumar Deptartment of Electrical and Computer Engineering, University of South Alabama, Mobile, AL.

The significance of using nano-phase ceramic materials is the benefit of increased performance for metal properties with respect to strength, toughness, toughness and ductility at elevated temperatures. In this work we propose to develop a self-lubricating nano-composite material comprising of nanolayers of soft high temperature lubricating material \(\text{ZnWO}_4\) on hard wear resistant matrix of WN. WN is known to be a wear resistant at elevated temperatures and \(\text{ZnWO}_4\) is a high temperature adhesive lubricant. WN films are deposited on Si(100) substrates by pulsed laser deposition (PLD) technique in nitrogen atmosphere. Then the \(\text{ZnWO}_4\) lubricant layers are coated by laser ablation of \(\text{ZnWO}_4\) target in oxygen atmosphere. The composite coatings are prepared at various temperatures and pressures, so as to optimize the parameters to get good crystalline phase of \(\text{ZnWO}_4\) coatings. The composite coatings are characterized by Raman spectroscopy, x-ray diffraction, scanning electron microscopy and atomic force microscopy to study their morphology and crystallinity. The mechanical properties such as the modulus of elasticity and hardness are evaluated by the nano indentation technique. This research is supported by NSF-DMII 0900458 MRSEC 1599 Fall Meeting Symposium L. Fundamental Mechanism of low-energy beams-modified surface growth and processing. Enhancement in the growth of textured HFCVD diamond coatings on modified Ti-6Al-4V substrate by eximer laser processing Mihail T. Gouriev, M. Vedavyas, G. S. Kharkal and Ashok Kumar Department of Electrical and Computer Engineering, University of South Alabama, Mobile, AL-36688, USA Currently, a major focus in diamond film technology is on the chemical vapor deposition of diamonds on metal substrates, for enhancing the durability of widely used metals. For a number of reasons, high quality diamond coatings are difficult to achieve on metal surfaces. In this work we address the studies of enhancement in diamond growth on Ti-6Al-4V metal alloy by modifying the surface using the eximer laser ablation technique, prior to deposition of diamond. Ti-6Al-4V is chosen for its technological importance in aerospace industry, dental and bioimplant applications. Analysis of the structures of the films is done by using X-ray diffraction, scanning electron microscopy and Raman spectroscopy. Ablation of the alloy by eximer laser pulses produces periodically hill/valley structures on the surface, thus increasing the density of diamond nucleation and film adhesion. The roughness of the alloy surface was measured to be in the 0.5 - 1.0 mu range with an average distance between peaks of the hill/valley structure measuring 1.5um. This research was supported by Alabama NASA EPSCoR program.

F5.37
COMPLEXES OF Cu(II) WITH POLYVINYL ALCOHOL AS PRECURSORS FOR THE PREPARATION OF Cu(II)/Pd(II) NANOCOMPOSITES.
Andrey A. Eliseev, Lidia I. Scholven, Alexander I. Zhizh, Alexey V. Lukashin, Konstantin V. Tomishievich, Alexei A. Vertegel, Higher School of Materials Science, Moscow State University, Moscow, RUSSIA.

Cupric oxide (CuO) nanoparticles have been prepared in amorphous SiO\(_2\) matrix using a novel variant of sol-gel technique. The method is based on the polycondensation of CuO and PdO (tetra(tert-amyl)oxide) in the presence of an aqueous solution containing complex of Cu(II) with polyvinyl alcohol (CuPVA). Studies of the gelation kinetics show that the process is the first order reaction with respect to CuPVA. After gelation, polymeric complexes containing several thousand Cu atoms each are incorporated into the silica network forming a precursor, which is then freeze-dried and annealed in oxygen to get rid of organic components. The freeze-dried gels and the annealed products were characterized by XRD, X-ray photoelectron spectroscopy, ESR, and TEM. The formation of CuO nanoparticles was confined by electron diffraction studies. The size of nanoparticles can be controlled by varying the concentration of CuPVA in initial solution and using polyvinyl alcohol with different molecular weight. CuO nanocomposites are characterized by high specific surface area as measured by capillary absorption of nitrogen at 77 K, suggestin its possible use in catalysis.

F5.38
LIGAND, VISCOSITY, AND POLYMER STRUCTURAL EFFECTS IN THE SYNTHESIS OF SURFACE METALIZED POLYMNAMIDE. J. V. Kryder in situ STRETCH REDUCTION OF SILVER(I) COMPACT SILVER. Robin E. Southward, National Research Council, Langley Research Center, National Aeronautics and Space Administration, Hampton, VA; Elizabeth Cornell, Christopher J. Davis, David W. Thompson, Department of Chemistry, The College of William and Mary, Williamsburg, VA.
Metallized polymeric films are commonly prepared by physical vapor deposition (PVD); however, poor adhesion results with passive metals. We report an in situ single-stage preparation of silver(I) complexes in solutions of polyvinyl alcohol for the fabrication of silver-polyimide films which are highly reflective and conductive and which exhibit superb adhesion. Silver(I) complexes of tris(acetylacetonato) and the bis(diketonato) unis, trifluoromethyl acetate, thienyltrifluoracetone, and hexafluoropropyl acetone, with polyvinyl alcohol and dimethyloxide are cast as films. Thermal curing to 300°C effects (1) reduction of silver(I) complexes to silver, (2) crosslinking among these six silver(I) precursors for the surface metallization of three polyimides at differing viscosities, and (3) a surface texture. The relationship between structure and properties will be discussed.

F5.40 FLEXIBLE INORGANIC/ORGANIC HYBRID SHEETS FABRICATED FROM METAL ALCOXIDES AND PLOIDNITROXIDE. Noriko Yosumoto, Ikuko Yoshinaga and Shingo Kikumori, Nippon Steel Corporation, Advanced Technology Research Laboratories, JAPAN.

Flexible inorganic/organic hybrid sheets were synthesized from polydimethylacrylate and chemically modified metal alkoxides. The chemical modification of metal alkoxides formed no precipitate in the synthesis process, resulting in homogeneous and transparent hybrids that contain various inorganic components derived from Al, Ti, Zr, and Nb alkoxides. The inorganic species derived metal alkoxides were less than several nm sizes, because any inorganic particles were not observed by TEM even with 1 M magnifications. The hybrids also exhibited excellent flexibility with the storage modulus of 100-7 Pa. The flexibility was constant up to about 300°C. Especially, we succeeded in fabricating large sheets of A4 size for the hybrids containing the organic component derived from Zr alkoxide. The incorporation of nanoparticles of titania prepared by hydrolysis of Ti alkoxide into the hybrid was also carried out to improve the surface mechanical properties. The tensile strength showed an abrupt increase and leveled off at a low particle content of 2.7 vol %.

The DSC experiments revealed that the DSC peaks for crystallization and melting of PDMS in the hybrid were reduced and shifted by addition of the particles. The reduction and shift of the DSC peaks are due to the weaker mobility of PDMS. The decrease in mobility is attributed to the strong interaction between the particles and PDMS, possibly leading to a change in the hybrid structure for the increase in tensile strength. Research supported by NEDO, under the Synergy Ceramics Project of the ISTF program promoted by AIST, MITI, JAPAN.

F5.41 SOFT CHEMICAL DESIGN OF TRANSITION-METAL-OXIDE / CLAY LAYERED NANO COMPOSITES. Kiyoaki Hisi, Shuji Narita, Shuji Kudo, Kenji Myoshin, Toshiki M missionaries, Department of Material Process Engineering and Applied Chemistry, Akita Univ., JAPAN.

Metal / insulator layered nanocomposites attract great interest from not only scientific but also industrial aspects. For constructing such composites, layered transition metal oxide and clay minerals are expected to be the conductor and insulator parts of the structure. Here we would like to show a new synthetic approach based on soft chemical techniques to form a layered nanocomposites wherein transition metal oxide and silicate layers are alternately stacked with nanometer order of period. The processing involves the two-dimensional polycrystallization of metal hydroxide monolayers through hydrolysis of cations (intercalation) and oxidation of the hydroxide layers with aqueous NaClO solution (dimin sulfuric reaction). This successive processing affords a new expanded structure of thickness 1 of the order of 10 nm. The composition of the c-direction was determined with the aid of one-dimensional neutron analysis, indicating that ⁴⁺ is sandwiched by two nanolayers of hydrated alkali cations in the interlayer space of the clay. The relation between structure and properties will be discussed.

F5.44 CHARACTERIZATION OF Pt/TOO BOX NANO COMPO SITE FILMS PREPARED BY CO-SPUTTERING. Shoichi Sanuki, Nao Yonemoto, Naoi of Research Institute, Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki, JAPAN; Michio Koinuma, Masayuki Naguchi, Yoshiaki Matsuo, Koyama University, Dept. of Applied Chemistry, Kugohmura, JAPAN.

It is well known that Pt/TOO BOX composite has been used as the photocatalyst for decomposition of water. Pt/TOO BOX composite has been prepared by various methods such as sol-gel methods and thermal decomposition. In this study, we report the synthesis of nanocomposite films (platinum nanocomposites dispersed in TOO BOX films) by co-sputtering method and its photocatalytic properties of these films were investigated. TEM, XPS and XRD measurements of the films revealed that the Pt/TOO BOX nanocomposite films consist of Pt metal nanoparticles in the matrix of rutile-type TiO₂. The size of Pt nanoparticles in the composite films increased with the heat-treatment temperature. The Pt nanoparticle size in the film with a Pt/TOO BOX atomic ratio of 0.18 decreased to 5 nm. The absorption edges of the Pt/TOO BOX nanocomposite films in aqueous solutions were investigated. Anodic photocurrents of Pt/TOO BOX nanocomposite at 1.2 V vs. Ag/AgCl were observed at the wavelength of 400 nm, which was much lower than that of TiO₂. Luminescence emission at 700 nm was also observed by UV excitation from the Pt/TOO BOX nanocomposite films at room temperature, and the optical properties of Pt/TOO BOX nanocomposite films were much different from

F5.42 STRUCTURAL STUDIES OF NANOPHASE SILICA-CHITOSAN METAL AEROGELS. Xiaogang Hu, Shangji Ji, William M. Risen, Jr., Brown University, Dept. of Chemistry, Providence, RI; David Pickles, Cornig Inc, Cornig, NY; Kenneth Littrell, Argonne National Lab, NBS, Argonne, IL.

Aerogels containing silica, the bio-derived polymer chitosan, and transition metal ions have been studied by spectroscopic, microscopic, optical, and neutron scattering methods to determine the structural nanoscale and molecular scale features of their structures. The optical and spectroscopic investigations show that the chitosan is incorporated as an integral component of the nanophase, and that the metal ions, including Rh, Ru, Cu, Ni, or Cu, are coordinated to it. The transmission electron microscopic (TEM) and small angle neutron scattering (SANS) studies have served to elucidate the nanophase structure itself. The TEM work will be presented in both direct and replication mode. The SANS data were obtained in the range of q values of 0.001 to 0.5 (reciprocal Angstrom), and analyzed in the context of the TEM data by several approaches. In the log q range -1.8 to about -0.8, the data show a power law correlation. The data from these studies will be interpreted in terms of the relation between particle size and a correlation length associated with collections of particles.
those of TiO₂. It appears that interfacial or surface states between homogeneously dispersed Pt nanoparticles and TiO₂ matrix produce new energy levels within the bandgap of TiO₂.

F5.45
RADIATION-INDUCED CRYSTALLIZATION AND
AMORPHIZATION OF Si NANOPARTICLES, EMBEDDED IN SiO₂.

Due to the quantum-size effect Si nanocrystals (Si-nacs) can emit strong visible light, therefore they are widely considered as the most promising candidates for future integrated optoelectronics. In spite of the extensive studies of Si-nacs, the physical aspects of their synthesis, processing and stability are still not clarified. This report describes the unusual behavior of Si nanoparticles under irradiation. The Si-nacs have been synthesized by the RIE technique using the 750 nm thick SiO₂ layers subsequent annealing at 1150°C for 30 min. Then the layers were irradiated with the 30-310 keV He ions to the doses of 1x10^13-3x10^16/cm² or with the 400 keV, 60 A/cm² electron beam in the Hi-Res column for 2-80 min. In situ TEM, photoluminescence (PL) and HREM were used for the characterization. Low dose room temperature irradiation caused the decrease in the PL intensity, but the number of Si-nacs after irradiation was found to be increased. Both effects were observed, when the ion and electron doses provided about 1 displacement/Si-nc. Further irradiation up to ~0.1 displ./atom (~500 displ./Si-nc) amorphized Si-nacs. This contrasts with the known results on the bulk Si, in which irradiation never led to amorphization. After the low dose irradiations (~500 C/cm²) amorphous Si-nacs were restored to the initial state, while the crystallization of the amorphized Si-nacs needed >500 C/cm². When annealed at 1150°C, the layers with the restored Si-nacs showed extraordinarily high electron emission currents much stronger light, than the as-prepared at 1150°C layers. It was shown that Si-nacs may be obtained with no additional annealing if Si ions are implanted in SiO₂ at the target temperature as low as 600°C. In the case of electron exposure the elastic losses of particles are suggested to play more important role than ionization and thermal processes.

F5.46
PREPARATION OF HIGHLY ORDERED MESOPOROUS THIN FILM WITH ALKYLMETHYLAMMONIUM (C₃H₇N⁺)³⁺;
Yasumoto Goto, Japan Chemical Innovation Institute, Gifu, JAPAN; Noriaki Sugimoto, Yoshiaki Fujishima, Toyoda Central R&D Labs. Inc., Aichi, JAPAN; Yoshihiro Kubota, Yoshihiro Sugai, Gifu Univ., Dept of Applied Chemistry, Gifu, JAPAN.

Much attention has been paid for mesoporous molecular sieves because of its application for sensor, adsorbent, and catalyst. The morphology of mesoporous molecular sieves is also an important factor for the applications. We synthesized the highly ordered mesoporous thin films with alkylvtrimethylammonium (C₃H₇N⁺)³⁺. We prepared the gelatinous powder obtained from the chloroform/methanol/water mixture with the different acid condition, in which glass plates were dipped and dried at 373K for 1 hour. The glass plates with mesoporous silica film were put by calcination at 773K for 6 hours. The thickness of the thin films was 100-500nm. The samples were studied by XRD, TEM, and nitrogen adsorption isotherms. The arrangement of mesopores was dependent on the Surfactant/Si ratio. The hexagonal (P6/mmm) arrangement was observed, when Surfactant/Si ratio was 1/10. In most samples, the Surfactant/Si ratio to 1/6/10, the cubic (Pmcn) arrangements were observed. A stainless vessel for the measurement of the nitrogen adsorption isotherms of thin film on the substrate was designed. It was found that mesopore arrangements in the films was more regular than that in the powder samples prepared by the same acidic synthesis condition. The films with 1.535nm of pore diameter were also made by using surfactants with various chain length. The pore size distribution was also narrow. We will also report the catalytic properties.

F5.47
ELECTROLUMINESCENCE DEVICES WITH CdS AND CdSe-Mn
NANOPARTICLES AND POLYMER BLENDS.
Ch. Brugger, S. Thach, G. Leman, Institut fuer Festkoerperfysik, Technische Universitaet Graz, AUSTRIA; M. Lul, P.N. Prasad, Photonics Research Laboratory, State University of New York at Buffalo, Buffalo, NY.

We have investigated the photophysical properties of surface capped CdS and CdSe-Mn nanoparticles in the form of spin-coated thin films of the pure nanoparticles and nanoparticle - polymer blends. The organic capping reagent is p-thiobenzophenone. Electroluminescence (EL) devices were fabricated and characterized by their current / voltage characteristics and emission parameters. This work concludes the first report on Mn doped CdS nanoparticles applied in EL devices with a single layer device structure (ITO/CdS/Mn/AI).

Photoluminescence (PL) and EL excitation measurements were performed on CdS-Mn nanoparticles in pyridine dispersion and on films. The PL excitation spectrum shows a narrow peak at 390 nm. Excitation at this wavelength yields a broad PL spectrum spanning from about 450 to 700nm, which is dominated by a strong emission band at 585nm. This emission is attributed to transitions involving Mn levels in previous works. The EL emission is shifted to the red compared to the PL emission spectra. The characteristics and performance of these new types of EL devices were presented and discussed. One of us (Ch. Brugger) would like to gratefully acknowledge the financial support provided by a Stipendium fuer kurzefristige wissenschaftliche Arbeiten im Ausland and the Research Foundation of SUNY.

F5.48
MOSBAUER AND MAGNETIC INVESTIGATION OF AEROGEL AND XEROGEL NANOCOMPOSITE MATERIALS CONTAINING IRON OXIDES. Giorgio Conto, Andrea Baliggi, Giorgio Spagna, Carnegie Univ., Dept of Physics, Pittsburgh, PA; Matteo Gatteschi, Claudio Sangregorio, Florence Univ., Dept of Chemistry, Florence, ITALY; Carla Canina, Maria Francesca Casula, Anna Correra, Anna Musini, Cagliari Univ., Dept of Chemical Science, Cagliari, ITALY.

Nano composite materials constituted of iron oxide nanoparticles dispersed into an amorphous silica matrix have attracted technological and scientific attention since it is possible to stabilize magnetite which presents interesting magnetic and catalytic properties. These nano composite materials can be prepared using a simple solgel method starting from TEOS and iron nitrate as precursors. Depending on the adopted drying conditions samples with very different surface areas can be obtained. In particular, aerogels with a high surface area and pore volumes can be obtained by performing the drying steps under supersaturated condition of volatile solvents, in which the internal pore structure of the aerogels is lost, can be obtained by slowly removing the solvent. In this paper aerogel and xerogel samples containing the same amount of iron oxide and treated at the same temperatures are studied. The superparamagnetic behavior of the samples is investigated using magnetic susceptibility measurements, magnetization curves and Mössbauer spectra collected at different temperatures. All these measurements show the variation of the effective magneton content as a function of thermal treatment. Moreover, the comparison between aerogel and xerogel samples allows to understand the effect of the surface area on the abundance of magnetite formation.

F5.49
Z-CONTRAST SCANNING TRANSMISSION ELECTRON MICROSCOPY AS A TOOL. FOR INTERFACE ANALYSIS IN NANOCRYSTAL-POLYMERIC NANOCOMPOSITES.
Andrew V. Kucharski, Todd Kippeny, Meg M. Erwin, Sandra J. Roseenthal, Vanderbilt University, Dept. of Chemistry, Nashville, TN; Stephen J. Pennycook, Oak Ridge National Laboratory, Solid State Division, Oak Ridge, TN.


F5.50
ATOMIC FORCE MICROSCOPY INVESTIGATION OF THE
MORPHOLOGY OF HYBRID ORGANIC-INORGANIC
COMPOSITES.
Lee C. Zhao, Anthony B. Brennan, Univ. of Florida, Dept. of MS&E, Gainesville, FL.

We present the use of phase detection imaging by the atomic force microscope (AFM) to enhance the morphology of novel organic-inorganic hybrids. Using the sol-gel process, we synthesized hybrid organic-inorganic composites from tetramethoxysilane (TMOS), and poly (tetramethylene oxide) (PTMO). These composites contain a mixture of silica domains and finely distributed inorganic components. They were synthesized under acid catalyzed and base catalyzed conditions to generate different morphologies. Previous research has shown that
samples made under base catalyzed conditions demonstrate more phase separation than acid catalyzed samples. These samples were fractured, and analyzed using tapping mode AFM. We used phase detection imaging to distinguish between the inorganic silicate phase and the organic polymeric phase. The AFM data showed significant differences in sample morphology due to the different synthesis conditions. Dynamic mechanical spectroscopy was also performed to correlate with the AFM data. We also studied the effect of using different molecular weight PTMO on the morphology.

F5.51
MODIFIED SOL-GEL SYNTHESIS OF VANADIUM OXIDE NANOCOMPOSITES CONTAINING SURFACANT IONS
Aruhny Dhibikey, SUNY-Binghamton, Dept. of Chemistry, Binghamton, NY; M. Stoney Whittingham, SUNY-Binghamton, Dept. of Chemistry, Binghamton, NY.

Recently, there has been much interest in creating new layered metal oxides. Vanadium oxides may be used as sorbents, catalysts, and cathodes. The modified sol-gel technique allows for some control towards the final structure of the compound. Using this technique, new layered vanadium oxide compounds, containing the surfactant dodecylphosphonic acid, have been synthesized. The compounds were analyzed using FTIR, XRD, TGA, and NMR. VO_4PO_3C_12H_32 is the general formula of the layered products with a layer spacing of about 3.7 Å. The synthesis, composition, and structure of these compounds will be discussed. This work was supported by The National Science Foundation.

F5.52
OPTICAL PROPERTIES OF SILICON NANOCRYSTALS PREPARED BY Si ION IMPLANTED SO_2 LAYERS. Z.P. Weng, K. Ding, H.X. Han and G.H. Li, National Laboratory for Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, Beijing, CHINA.

The samples were prepared by Si ion implanted SO_2 layers grown on n- Si (100) substrate and annealed at 480 - 1200 °C in N_2 atmosphere for 30 min. PL and Raman scattering spectra and their dependence on annealing temperature were measured at the room temperature. The PL peaks observed in as-implanted sample originate from the defects in SO_2 layers caused by ion implantation, which disappear after thermal annealing of 800°C. The PL peak from silicon nanocrystals was observed when the thermal annealing temperatures are higher than 900°C. The PL peak is redshifted to 1.7 eV and its intensity reaches maximum at the thermal annealing of 1100°C. Raman scattering spectra were measured at the right angle scattering configuration. The results show that only optical phonon mode from Si substrate was observed below the annealing temperature of 800°C, and the characterized scattering peak of silicon nanocrystals was observed when the annealing temperature is higher than 800°C. The size of silicon nanocrystals after thermal annealing of 1100°C is about 3 - 4 nm as estimated from the position of the characterized Raman peak of silicon nanocrystalline. After the thermal annealing of 1200°C, the PL peak decreased. The characterized scattering peak of silicon nanocrystals is disappeared and a Raman peak centered at about 490 cm^{-1} appears which is similar to the optical phonon peak of nanocrystalline Si. Thus we suppose that silicon nanocrystals can not bear the thermal annealing at 1200°C.

F5.53
NANOCOMPOSITES OF TITANIUM DIOXIDE AND CONJUGATED POLYMERS. Shujin Yi and Samsun A. Jenekhe, Department of Chemical Engineering, University of Rochester, Rochester, NY.

Dispersions of nanoparticles of inorganic semiconductors in polymers are of wide interest for applications ranging from light-emitting devices to photovoltaic cells. Because titanium dioxide is an n-type semiconductor, its nanocomposites with conjugated polymers can exhibit enhanced charge generation at the photodiodes due to photoinduced electron transfer between the components. We have used a new synthetic method to prepare new titanium dioxide/poly(pyrrole) nanocomposites for optoelectronic applications. Characterization of their morphology by scanning electron and transmission microscopy electron microscopes showed that the titania dioxide phase forms mesosporous one-dimensional structure in composites of low concentration (less than 15 wt % TiO_2) and 90-120 nm diameter spherical particles. The optical absorption and photoluminescence spectra depend on the nanocomposite composition. Among the unusual photophysical properties of the TiO_2/polymer composites is a unique fluorescence in luminescence, which can be understood as a result of reduced interchain exciton quenching in the nanocomposites.

F5.54
INSTITUTE STUDIES OF POLYMER-Carbon NANOtube COMPOSITE DEFORMATION. Dali Qian, Elizabeth Dickey, Department of Chemical and Materials Engineering, University of Kentucky, Lexington, KY; Terry Rustad, Rodney Andrews, Fredrick Delorshire, Center For Applied Research, Lexington, KY.

Carbon nanotubes are known to have both high moduli and tensile strengths along the tube axis. Potentially, they could be used as a reinforcing phase in polymer matrices to tailor the mechanical behavior of polymer materials. The utility of the nanotubes as a reinforcing phase depends strongly on the ability to disperse the nanotubes homogeneously throughout the matrix without destroying the integrity of the nanotubes. Furthermore, interfacial bonding between the nanotube and matrix is necessary to achieve load transfer across the interface. Here we investigate polymer matrices (polyethylene and polyethylene) reinforced with multiwall or single wall carbon nanotubes. Several loadings of nanotubes were studied, including 1% and 5%. In the polyethylene matrix, 1% multwall nanotube additions resulted in a 25% increase in ultimate tensile strength. The structure, reaction and real-time deformation of the composites were studied by transmission electron microscopy (TEM). Conventional TEM was used to quantify the dispersion of nanotubes throughout the matrix and to define preparation conditions that lead to a homogeneous dispersion. In-situ TEM deformation studies provided information regarding deformation mechanisms and interfacial bonding between the carbon nanotubes and polymer matrices. Correlations between the TEM and mechanical properties data will be discussed. This work was supported by a National Science Foundation MRSEC (DMR-9809886).

F5.55
SYNTHESIS AND CHARACTERIZATION OF Fe_3 Al_2 O_7 NANOCOMPONENTS. Armando Santos, Waldemar A.A. Maedero, José D. Aciord, Laboratório de Física Aplicada, CDTN / CNEN, Belo Horizonte, BRAZIL; Alexandre D.C. Viego, João E. Schmidt, Instituto de Física, UFURGS, Porto Alegre, BRAZIL.

We have investigated the synthesis and the structural and magnetic properties of Fe nanoparticles embedded in Al_2 O_3 matrix, a granular nanocomposite prepared by sol-gel processing. Samples with volumetric Fe content ranging from 16 to 50% were obtained starting from Al nitrate and Fe sulfate as precursors. The preparation method results initially in a mixture of Fe_3 O_4 into metallic Fe was done by calcination at 800°C followed by reduction at 600°C, for 2 hours, in H_2 atmosphere. The obtained powder samples were characterized by X-ray diffraction, Møssbauer spectroscopy and vibrating sample magnetometry. Our Møssbauer and X-ray diffraction results indicated the following phases after reduction: α-Fe, the main phase, α- and γ-Fe_3 O_4, Fe_3 O_4 and some Fe_3 Al_2 O_7. For the investigated system, Fe reduction rate was very sensitive to the sample porosity and with the applied method we have obtained reductions of the Fe atoms into metallic Fe ranging from 60 to 81%, preserving the mean diameter of the Fe_3 O_4 nanoparticles between 60 and 70 nm. VSM measurements at room temperature resulted in coercivities around 450 Oe and saturation magnetization between 60 and 100 emu/g. Magnetic measurements are in development. Preliminary measurements for a sample with 31% metallic Fe (and about 50% total Fe) reveal ΔH/R equal to 2.2% at room temperature. Financial support: CNEN, CNPq, FAPEMG and FAPERGS.

F5.56
FABRICATION OF LAYERED NANOCOMPOSITE CERAMICS FOR SENSING AND ACTUATING. Masayasu Arizono, Yoshinobu Fujishiro, Hiroaki Taki, Joocho Moon, National Industrial Research Inst. of Nagoya, JAPAN; Sergei Breidikhin, Inst. of Solid State Ionics, Russian Academy of Science, Chernogolovka, RUSSIA; Koichi Niinuma, IRS, Oskm Univ., Oskm, JAPAN.

A layered nanocomposite ceramics was fabricated to realize materials devices, which reveal novel functions such as remote sensing, remote actuating and self power generation. Nanocomposite effect is expected for its application based on physical phenomenon such as single domain structure, nanocrystal effect, spin electronics and so on. On the other side, development of the nanocomposite processing enables us to obtain syngmatic enhancement of functional and structural properties leading to widen application. Layered nanocomposite of an ionic conducting material involving magnetic nano-dispersions with a structural ceramics revealed integrated functions of remote sensing of applied stress and fracture, and self actuating by magnetic induced electronic response with improved mechanical properties. The nanocomposite is applicable as a sensor and an actuator in severe circumstances.

F5.57
Transferred to F1.9.

F5.58
SPECTROSCOPIC ELLIPSOGRAPHY OF NANOCOMPOSITE SiH
Spectroscopic ellipsometry study of Si:H layers formed by high fluence hydrogen implantation (up to $3 \times 10^{17}$ cm$^{-2}$) with a pulsed 30 keV proton beam with current up to 40 mA/cm$^2$ was carried out in the present work. The Si:H silicon films were characterized also using transmission electron microscopy, secondary ion mass spectroscopy, and infrared spectroscopy. Hydrogen solubility in crystalline silicon is low but ion implantation allows introducing of $2 \times 10^{17}$ cm$^{-2}$ of the hydrogen atoms or even more in thin silicon layer. High defect concentration in amorphous hydrogenic silicon semiconductor is the formation of film with structural properties similar to porous silicon produced by electrochemical anodization. The transformation of optical properties of Si:H films during tempeibration in temperature range investigated is in the work. Structural characteristics have allowed us to distinguish the relative contributions of hydrogen filled voids, amorphous and crystalline zones to optical properties of obtained layers

**F5.50 UNDERSTANDING THE SECOND HARMONIC GENERATION OF LIGHT FROM NANO-METAL COMPOSITES VIA LOCAL FIELD ENHANCEMENT FACTORS.** Marie Sandrock, Colby A. Foss Jr., Georgetown University, Department of Chemistry, Washington, DC.

We have synthesized two sets of nanocomposites of differing metal volume fractions via electrodeposition of gold into porous aluminum oxide membranes.1,2 Within each set, both centrosymmetric and non-centrosymmetric particles were produced. A co-linear microfabrication technique was investigated. We discuss comparisons of the experimental linear optical spectra of gold non-centrosymmetric particle structures to that of symmetrical gold particle and box-particle structures. We intend to correlate the intensity of the nonlinear response to that of the respective linear spectra. In general, increasing the rod size leads to an increase in the SHG intensity produced from the composite materials, regardless of symmetry. Additionally, we find that SHG intensities do not vary greatly between different geometries of centrosymmetric particles (at constant metal volume fraction), while the linear spectra are quite different. Because our method of template synthesis allows for the close examination of our composite materials in terms of shape, size, and symmetry, we can evaluate the SHG response in terms of differences in local field enhancements of magnetic dipole and quadrupole modes.2 Reference 1: Sandrock, M.L.; Fiedl, C.D.; Geiger, F.M.; Foss, C.A., Jr., J. Phys. Chem. B, 103, 2068 (1999). 2: Sandrock, M.L.; Foss, C.A., Jr., J. Phys. Chem. B, submitted. 3: Leitner, Alfred, Molecular Physics, 2, 197 (1990).

**F5.60 THE THERMAL RESISTANCE OF ALUMINUM/TITANIUM MULTILAYER THIN FILMS AND THEIR INTERFACES.** Daniel Josell, Eduardo J. Gonzalez, John E. Borevich and Grady S. White, National Institute of Standards and Technology, Gaithersburg, MD.

As the individual layers within electronic materials become thinner, heat flow predictions based on bulk properties become increasingly inaccurate. This is especially true in the transport properties of thin film materials which can differ from those of bulk materials. In addition, the thermal resistance associated with interfaces between layers becomes more significant as the layers become thinner. Accurate modeling of heat flow in future devices will require at least empirical understanding of these individual effects. We have, therefore, measured the thermal diffusivity (thermal conductivity divided by specific heat per unit volume) of electron beam evaporated Al/Ti multilayer thin films that were 3 μm thick, each with a different Al/Ti bilayer thickness (between 5 nm and 80 nm). The properties of homogenous Al and Ti films, also 3 μm thick, were also obtained. Thermal diffusivities were measured both perpendicular and parallel to the plane of the layers using the Impulse heat transfer technique. The interface thermal resistance was determined from the dependence of the thermal diffusivity on the bilayer thickness. Copper thin films ranging between 1 cm and 5 μm thick were also measured.

**F5.61 SPONTANEOUSLY PROPAGATING REACTIONS IN NANO SCALE MULTI LAYER FOILS.** Tim Wehr, Dept. of Materials Science & Eng., Johns Hopkins Univ., Baltimore, MD; Omar Knio, Dept. of Mechanical Eng., Johns Hopkins Univ., Baltimore, MD.

This presentation describes the development of novel, self-propagating exothermic reactions in nanoscale multilayer foils. The reactive foils are fabricated by vapor depositing alternate layers of materials that have high heats of mixing, such as Al and Ni or Nb and Si. The individual layers are only nanometers thick, but each film contains hundreds of these layers and has a total thickness between 10 and 100 microns. The thick foils are easily removed from their substrates after deposition, and their exothermic mixing can be started at room temperature with a simple external energy source. The reactions propagate into greater speeds greater than 5 m/s, and they reach final temperatures as high as 1000 C. During the talk we will describe how these foils can be used as rapid heat sources for joining and cutting, and we will review experimental characterization of the heats, the velocities, the temperatures, and the transformations of the reactions.

For example, we will show that reaction velocity depends strongly on the concentration heat that drive the reaction and the individual layer thicknesses that determine diffusion distances. These experimental results will be compared with extensive predictions from analytical and numerical models.

**F5.62 HIGH-PRESSURE SYNTHESIS OF BISMUTH NANO-COMPOSITES FOR THERMOELECTRIC APPLICATIONS.** Tito E. Hailer and Pierre Constant, Howard University, Washington, DC; Michael Graf, Department of Physics, Boston College, Chestnut Hill, MA; Colby A. Foss, Department of Chemistry, Georgetown University, Washington, DC.

We have fabricated Bi nanowire array composites with wire diameters from 30 to 200 nm by high-pressure-injection of Bi melt into porous anodic aluminum templates. The composites are dense, with Bi volume fractions in excess of 90%. The parallel Bi nanowire terminal leads on both sides of the composite in the Bi bulk. We have employed scanning electron microscopy, energy dispersive X-ray Spectroscopy, and X-ray diffraction to characterize the composites. We are interested in the potential application of these composites as a thermoelectric device. In particular, the alloys are the best thermoelectric materials at moderately low temperatures (~100 K). It has been suggested that microengineering traditional thermoelectric materials into composites may lead to improved performance because of the reduction of phonon thermal conductivity. Also, the thermoelectric figure of merit may be dramatically increased over that of the bulk because of the increase of the electronic density of states that occur in low dimensional systems.

**F5.63 ROOM TEMPERATURE COERGENCY ENHANCEMENT IN MECHANICALLY MILLED FERROMAGNETIC ANTI-FERROMAGNETIC COMPOSITES.** J. Sart, J. Nogues, X. Amils, S. Schiffrich, J. S. Muñoz, MD, Baro, Dept. de Física, Univ. Autonoma de Barcelona, Bellaterra, Spain.

Mechanical alloying has been used to induce exchange interactions in for example remanence enhanced hard magnetic materials [1] or in giant magnetoresistance alloys [2]. We have used mechanical milling to induce an exchange interaction between ferromagnetic (FM) and antiferromagnetic (AFM) materials. By mechanically milling FM and AFM materials with Néel temperature, $T_N$, above room temperature the room temperature coercivity, $H_C$ of the FM material is markedly increased. In particular, Co has been mechanically milled with NiO ($T_N = 590$ K) and FeS ($T_N = 610$ K) in different conditions. A substantial increase in $H_C$ was found if the AFM/FM composite was field annealed above $T_N$, field cooled to room temperature. The increase of $H_C$ decreases above $T_N$. The dependence of $H_C$ on the annealing and measuring temperature indicate that the exchange bias [3] is the origin of the observed effect. This work was supported in part by CYCIT (MAT98-0739). J.S. thanks the DGU for his fellowship. [1] P.G. McCormick et al., Magn. Magn. Mater. 157/158 (1996) 7; [2] S.M. Thompson et al., Phil. Mag. B 98 (1998) 823; [3] J. Nogues and Ivan K. Schuller, J. Magn. Magn. Mater. 192 (1999) 265.

**F5.64 3-D PERIODIC NANO-COMPOSITES FOR METALLIC PHOTONIC CRYSTALS AND HETERO-STRUCTURES.** Anwar A. Zakhidov, Ray H. Baughman, Igor A. Udod, Lo-Min Liu, Zhejiang Chi, Research and Technology, AlliedSignal, Inc., Morrisville, NJ; Ilan A. Kheirullin, Mikhail E. Kozlov, New Jersey Institute of Technology, Newark, NJ; Nair Ebrah, Voly Z. Vardeny, Dept. Physics, University Of Utah, Salt Lake City, UT.

We have created highly porous nanomaterials and nanocomposites and nanostructured materials that are typically periodic at optical wavelengths and can be modeled in terms of two-component systems. In the first part of this talk we show that well-dielectric systems of this type demonstrate interesting optical properties in infrared bands, confirming the metallic photonic crystal structure of nanocomposites and the existence of a metallic photonic band gap below the plasmon driven cut-off frequency. In a second part, we discuss transport and thermoelectric properties, including...
suppression of thermal conductivity, and change of the temperature dependence of conductivity. With the aim to increase thermopower, we suggest the formation of heterojunction arrays between two components of semiconductor (SC) or metallic (M1/M2) nanocomposite networks. These arrays can be created so that substantial charge transfer occurs between components, creating a macroscopic defect that inhibits interface diffusion. Another way to create 3-D arrays of p/n junctions by non-homogeneous doping during a micro-molding process. The optimal design of such heterojunction arrays geometry and electronic bands matching are discussed following our recent theoretical and experimental work. For fabrication of 3-D superlattice nanocomposites, a simple method is developed using porous nanofluids of SC as a template for infiltration with second SC2 material. The fabrication steps include creation of porous nanofluid from SC material, with high melting point: either Si or Te, both being chemically stable in HF (which is used to dissolve the initial silic acid). As a second step, melt layer Bi as SC2 is infiltrated into SC1 inverted opal matrix either by high pressure or by a method from a melt of SC2. The obtained nanostructures are characterized by TEM. TEM optical reflectivity and low-angle X-rays, and show drastic changes of optical, thermoelectric and transport properties. On formation of a 3-D nanocomposite. *Research supported by DARPA grant DAAH07-05-1-0083.

F5.65 CORRELATION OF MICROSTRUCTURAL PROPERTIES WITH THE MAGNETORESISTANCE OF THE MAGNETIC NANOSTRUCTURED MULTILAYERS. Nenita Neamțu, National Institute for Research and Development in Microtechnologies, Bucharest, ROMANIA; M. Volmer, Transilvania University, Brasov, ROMANIA.

In this work, the influence of the roughness and microstructure of the layers at the interface of multilayers on the magnetoresistive properties has been investigated. We present some results on the anisotropic magnetoresistance of permalloy thin films and the giant magnetoresistance (GMR) of NiFe/Co/Cu/CoFe multilayer thin films, deposited by high vacuum evaporation and RF sputtering. The magnetic thin films have the thickness in the range 4-20 nm and the copper layer thickness was changed from 3 nm to 8 nm. The GMR in thin films was characterized using scanning electronic microscopy (SEM) and atomic force microscopy (AFM) for surface texture, grain size and roughness. Although the thickness of layers has leading part for magnitude of GMR effect, described in terms of spin dependent electron scattering, quality of interfaces, amount of bulk scattering centers and the roughness not by neglected. Our results showed that for the average grain size of NiFe thin films smaller than the intrinsic mean free path of the electrons, grain boundaries are an important source of electron scattering, even up to large film thickness and influence the giant magnetoresistance of multilayers.

F5.66 CHEMICAL VAPOR DEPOSITION OF TiC, WC, AND TiC/WC COMPOSITE THIN FILMS. Kathryn Versprille, Carmela C. Ammato-Wierd, University of New Hampshire, Materials Science Program, Durham, NH; Derk A. Wierd, Saint Anselm College, Dept. of Chemistry, Manchester, NH.

Recent progress in hard coating research suggests that nanocrystalline composite materials show improved hardness and toughness. This present study investigates the chemical vapor deposition (CVD) of TiC/WC multiphased nanocrystalline thin films. TiC is deposited using TiCl4, H2 (diluent and carrier gas), and CH4 and WC is deposited using W(CO)6, H2, CH4, and Ar as the carrier gas. The composition, morphology, and hardness of the individual TiC and WC films, as well as the co-deposited multiphased TiC/WC films, are characterized as a function of processing conditions, including reaction temperature, reaction pressure, residence time, and flow ratios.

F5.67 CRYSTALLIZATION BEHAVIOR OF A AMORPHOUS SiGe FILMS OBSERVED BY POSITRON ANNIHILATION. E. Edelmann, Technical University of Darmstadt, Dept. of Applied Physics, DARMSTADT, Germany; F. Borner, K. Krause-Relhaag, Halle Univ, Fac of Physics, Halle, Saaale, Germany; P. Werner, Max Plank Inst of Microstructure Physics, Halle, Saaale, Germany; R. Weil, Technion, Solid State Inst, Haifa, ISRAEL; W. Bauer, R. Buzas, p/n junction Thin Films and Ion Technology, Res Centre, Jülich, Germany.

The crystallization of undoped and boron doped Si1-xGex films, deposited on SiO2/Si(001) substrate by molecular beam in high vacuum at room temperature was studied by Doppler broadening spectroscopy using monoenergetic positrons. From X-ray diffraction (XRD) measurements, it is shown that the transformation of amorphous films starts at 600°C. This process was completed at temperatures higher than 850°C. It can be distinguished between three phases of crystallization. In phase 1 up to temperatures 550°C there is no crystalline lattice structure detectable. Phase 2 (600-800°C) shows a broad XRD spectra of crystalline SiGe. The crystallization is explained by the appearance of defects in the crystal structure and small crystal grain size. The films are fully crystallised in phase 3 after annealing higher than 850°C. With positrons as a probe an evolution process of the amorphous layer in phase 1 of the crystallization can be observed. In the amorphous SiGe layer, the positrons annihilate in the open volume of the amorphous matrix. The positrons are located in traps of very high density. This fact can be seen by the short positron diffusion lengths only 10 nm. A first evolution step can be observed at an annealing temperature of 150°C. A change in the annihilation line-shape parameter W shows that the positrons were located in open volume which is mainly surrounded by Ge atoms. A second change of the of the W parameter at a temperature of 250°C indicates an evolution of the amorphous layer to a more homogeneous distribution of the Si and Ge atoms being next to the positron traps. This fact could mean that a first close order structure of the SiGe lattice is coming into being. In conclusion, positron annihilation spectroscopy reveals that structural changes occurs in amorphous SiGe layers far below the crystallization temperature.

F5.68 A NEW METHOD FOR CALCULATION OF STRAINS IN NANOCOMPOSITE SEMICONDUCTORS. Vadim Yu. Milovskii, Inst of Chemistry, Dept of Quantum Chemistry, Kishinev, MOLDOVA.

A general approach is developed for calculation of both uniform and nonuniform strain fields periodically arranged on the surface of nanocomposite layers. The method is based on the use of sinusoidal functions as a basis. This allows the use of a simple and well-known method of the solution of the problems of the distribution of strains in composites. The method includes the solution of the problem of the distribution of strains in a composite of a nanosize layer, which is composed of the cores of two different materials. The method is based on the solution of the problem of the distribution of strains in a composite of two different materials. The method is based on the solution of the problem of the distribution of strains in a composite of two different materials. The method is based on the solution of the problem of the distribution of strains in a composite of two different materials.

F5.69 THERMALLY DRIVEN SHAPE INSTABILITY OF MULTILAYER STRUCTURES. Peter Trold, Jörg Hoffmann, Carsten Herweg, Jörg Schleining, Herbert G. Drayna, Universität Göttingen, Institut für Materialphysik, Göttingen, Germany; Dietmar Rudolph, Universität Göttingen, Institut für Küstenphysik, Göttingen, GERMANY.

The thermal disintegration of multilayers consisting of non miscible metals (e.g. Ni/Cu, Fe/Au, Fe/Ag, Cu/Co) was investigated by means of X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray microdiffraction (XRM). The single-layer thickness of one of the components was typically fixed to 10 nm, whereas the thickness of the second one was varied between 0.4 nm and 4 nm. The temperature of disintegration depends on the combination of the chosen metals, the microstructure of the interfaces, and the thickness of the thinner layer. Upon a critical thickness, the disintegration temperature rises proportional to the reciprocal thickness of the thinner layer. The minimum disintegration temperature ranges from 580°C to 1080 K for Fe/Au and Cu/Co multilayers, respectively. TEM pictures reveal a columnar growth of the films. These highly oriented columns with a width of some tens nanometers grow up to 800 nm in height, depending on the observed system. After disintegration the thinner layer has developed spiral secondary phases, which are concentrated at the grain boundaries between the columns. Therefore, after disintegration the nanoparticles are more or less well-ordered as a string of pearls perpendicular to the substrate. The driving forces of this process are governed by geometrical stress and by local variations of the curvature of the interfaces.
F5.70  BAND GAP ENGINEERING STUDIES WITH MESOSCOPIC GALLIUM NITRIDE COMPOSITES. Holger Weidler, Oliver Stenk, Roland A. Fischer, TU Braunschweig, Germany; Roland Schmelcher, Technische Universitat Darmstadt, Germany.

By varying the composition of specific ternary systems like AlN, GaN, and AlGaN by changing the thickness of the nitride layers, it is possible to tune the band gap of the material. This tunability offers applications in electronic and optoelectronic devices. The band gap engineering technique allows for the creation of novel materials with tailored optical properties.

F5.71  NOVEL METHOD FOR FABRICATION OF NONCRYSTALLINE COPPER COMPOSITES. A. Pharkya, A. K. Sharma, J. Narayan, Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC.

The formation of amorphous copper metal in the presence of copper oxide and other copper-containing compounds offers a promising approach for the fabrication of noncrystalline copper composites. These materials exhibit unique electrical and magnetic properties that can be exploited in various applications such as high-frequency electronics and magnetic data storage.

F5.72  COLOSSAL HOPPING MAGNETORESISTANCE OF GaAs/ErAs NANOCOMPOSITES. A.G. Petukhov, M. Foygel, and A. Chantre, Dept. of Physics, South Dakota School of Mines and Technology, Rapid City, SD.

We report our results on theoretical analysis of hopping magnetoresistance in quasi-2D nanocomposites of ErAs. The significant component of magnetoresistance is attributed to quenching of BMe in high magnetic fields. This component is significant for various applications including spintronics and magnetic memory devices.

F5.73  NANOCOMPOSITES IN THE SYSTEMS Fe1-x-OxFe2O4 AND MgO-MgFe2O4 PRODUCED BY MECHANICAL ALLYING. A. Huetta, R. Ordoñez, H.A. Calderon, H. Balomor, E. Regueiro, H. Yoo-Medina, Instituto Politecnico Nacional, Apldo. Mexico DF; M. Umesu, K. Terabe, Tokyo University of Technology, Tempuku-cho, Tokyo, Japan.

This investigation has been undertaken to develop novel magnetic materials with enhanced properties. The nanocomposites exhibit unique magnetic and electrical properties that can be tailored for various applications such as magnetic data storage and spintronics.

F5.74  RELATIONSHIP BETWEEN THERMALLY ACTIVATED ATOMIC DIFFUSION PROCESSES IN Co-Cu NANOSCALE GRANULAR FERRITE AND ELECTRIC/MECHANICAL PROPERTIES. F. Ronconi, P. Visser, G. Bondin, L.I.M. and Dept. of Physics, University of Ferrara, Italy; D. Bierer, L.I.M. and Dept. of Physics, University of Ferrara, Italy; L. Peretti and G. Turilli, Mater. Sci. and Eng., Ferrara, Italy.

The effect of thermally activated diffusion processes in Co-Cu multilayer granular films has been studied. The films show high magnetotransport and both their magnetic properties and the variation of resistivity as a function of reduced magnetization display features characteristic of granular solid, which is non-interacting superparamagnetic particles. Thermal liberation of different heating rates yields different results. However, a differential scanning calorimetry under Ar flow has shown that the dependence of the type of diffusing element on heating rate has been observed. The changes in composition have been detected by X-ray photoemission measurements performed at various depths inside the films.
SESSION F6 APPLICATIONS AND PROPERTIES OF NANOPHASE AND NANOCOMPOSITE MATERIALS - I
Chair: Kwang Leong Chey
Wednesday Morning, December 1, 1999
Salon F (M)

8:30 AM *F6.1 NANOSIZED SEMICONDUCTING OXIDE POWERS FOR THICK FILM GAS SENSORS: FROM POWDER PROCESSING TO ENVIRONMENTAL MONITORING. Enrico Testa, Universita' di Roma Tor Vergata, Dept. of Chemical Science and Technology, Rome, ITALY; Maria Cristina Carotta, Giuliano Martinelli, INFN, Univ of Ferrara, Dept of Physics, Ferrara, ITALY.

The surface properties become paramount for nanosized materials, making them particularly appealing in applications where such properties are exploited, i.e. in gas sensors. Grain size reduction is one of the main factors determining the device properties. Nanosized semiconducting oxides used for gas sensing. Sharp increases in sensitivity are to be expected when the grain size becomes smaller than the space-charge length. The development of reliable and selective gas sensors is strongly needed for the control and monitoring of pollutants for ambient air quality, because the methods currently approved by the existing standards need the use of costly analytical equipment that limits the number of monitoring locations. The improvement of gas sensors' performance can be achieved using nanostructured materials. Chemical routes such as sol-gel techniques and thermal decomposition of heteronuclear complexes have been used to prepare nanosized powders of n-type (TiO2 and In2O3) and p-type (LaFeO3 and SnFeO3) semiconducting oxide materials. Thick film gas sensors have been fabricated using these powders, printed on Inconel 90% alumina substrates, each 2x2 mm element being provided with a heater. An interdigitated contacts and a P-100 resistor for controlling the operation temperature. The structural analysis of the nanosized powders is considered in addition to that of the resulting films. The firing of the films has been performed in conditions able to keep grain size at nanometer level. Electrical responses to some major pollution gases (CO, NO, NO2 and O3) have been tested in the laboratory and in the field, compared with the internationally-standard analytical techniques. The array of prototype devices have been located at the same place of a conventional station of environmental monitoring. The results obtained allow us to consider feasible the cost-effective devices for such sensors for new, innovative stations for environmental monitoring.

9:00 AM *F6.2 STRUCTURE AND PROPERTIES OF SnO2-TiO2 NANOCRYSTALLINE FILMS FOR GAS SENSORS. Felix Edelman, Horst Hahn, Holger Hoeche, Technical University of Darmstadt, Dept. of Material Sci., GERMANY; Peter Werner, Max Planck Institute of Microstructural Physics, Halle, GERMANY; Albert Chack, Vassilikon Mikedelawili, Ghadi Eisenstein, Technion, ISRAEL; N. Busov, Institute of Chemistry and Theor. Chemistry, Uni. of Tübingen, GERMANY.

Thin films (50 and 500nm) of SnO2-TiO2 were prepared at 100°C on Si and glass substrates by metal organic sol-gel deposition (MB). before annealing in oxygen at 300 to 800°C. Particular attention has been given to the compensation of the oxygen non-stoichiometry in the oxide films (especially manifested in the SnO2-rich films). Apart from the higher-temperature oxidation, the use of situ atomic oxygen (which is the low-temperature layer-by-layer process) during the film deposition is used. TEM, XRD, RBS, SIMS, XPS, Raman and IR-spectroscopy were employed to analyse the structure evolution in the SnO2-TiO2 films. The as-deposited state, the films are amorphous. Crystalization occurs at temperatures (above 500°C) forming nanocrystalline grains. The problem of the spinodal decomposition of the SnO2-TiO2 under oxidation annealing is discussed first for the low-temperature annealing (especially the spinodal decomposition was demonstrated in SnO2-TiO2 system for monocristals and ceramics above 800-850°C). The effect of the film densification upon annealing is investigated and problem of oxygen gas permeability through oxide film is analysed. In conclusion, the electrical conductivity and sensing properties of the SnO2-TiO2 films in oxygen or reduction environment are presented.


A new type of screen printed dye-sensitized large solar cell (15cm x 15 cm) based on nanocrystalline TiO2 is described. It is the largest photo-electrochemical (PEC) cell that has been realized to date. The sensitization of thin (8-18 µm) films of TiO2 nanoparticles in contact with a non-aqueous liquid electrolyte. The cell has the potential to be a low cost, commercial, environmentally friendly, photovoltaic option. Surface and interface characterizations of the nanocrystalline PEC cells as well as electrical characterization, e.g., quantum efficiency and fill factor, have also been performed. The efficiency of these large commercial cells are compared to the laboratory-grade small PEC cells.

9:45 AM *F6.4 ELECTRIC CHARACTERIZATION OF THIN FILMS CONSISTING OF Ti-DOPED INDUML OXIDE NANOPARTICLES. Arnette Hults, Gunnar A. Nilsson, Uppsala University, Dept. of Materials Science, Uppsala, SWEDEN; A.W.M. de Loo, Chris van Dongen, Philips CPT, Eindhoven, THE NETHERLANDS.

In recent years there has been a growing interest in cheap and easy production techniques for transparent conducting films. Thin layers of tin doped indium oxide (ITO) have been prepared by （…） solution of nanoparticles. In order to study the sintering behavior of these ceramic particles the dielectric response function has been studied and given incidence XRD measurements have been performed. The grain growth starts at 1000°C and a much more prominent at 1250°C. However, the conductivity reaches a maximum below these temperatures. The results are compared with theory for grain growth of ceramic nanoparticles and of conduction mechanisms in nanocomposites.

10:15 AM *F6.5 CARBON NANOTUBE POLYMER COMPOSITES. Polukid M. Ajayan, Linda Schader, Rensselaer Polytechnic Institute, Department of Materials Science and Engineering, Troy, NY.

Carbon nanotubes should be the ideal reinforcing fibers for composites. They have high aspect ratios, are extremely strong individually and are very light. The goal of creating high strength, lightweight polymer composites using nanotube fillers has been pursued in recent years by many workers. Although nanotubes are ideal fillers, the effectiveness of the composite will depend on the interface between the filler and the matrix as this will govern the load transfer properties of the composites. In addition, the behavior of nanotube aggregates such as single-walled nanotube ropes and multilayered nanotube assemblies is markedly different from the idealized individual nanotubes which have been used in theoretical predictions. Our experiments (processing, characterization, mechanical testing, and Raman spectroscopy to monitor load transfer) on nanotube-polymer systems reveal several important features which could lead to the development of optimized composites. A summary of these results will be presented in this talk.

10:45 AM *F6.6 PREPARATION OF OPTICAL COMPOSITES. Leslie L. Isaac, CCNY/CCNY Graduate Center, Dept. of Chemical Engineering; Robert H. Allendo, Vladimir Petrovic, CCNY/CCNY Graduate Center, Dept. of Physics and New York State Center for Advanced Technology for Ultrafast Photonic Materials and Applications, BingPing Wang, CCNY/CUNY Graduate Center, Dept. of Chemical Engineering, New York State Center for Advanced Technology for Ultrafast Photonic Materials and Applications, Jinping Ying, Institute for Ultrafast Spectroscopy and Lasers, New York, NY.

Solid gel technology is used to prepare micron-size particles of Chromium(IV) doped materials, which show strong luminescence, as single crystals, in the 1-2 µm range. Examples of such materials are Cr3+-C6H5GeO3 and Cr3+-C6H5SiO4. The preparative process can be optimized to reduce the particle size to the sub-micron range and to obtain a narrow particle size distribution. Furthermore, optical composites can be prepared by dispersing the optically active particles into transparent glassy matrices. SiO2 and SiO2- TiO2 are used as the glass forming matrix materials.

11:00 AM *F6.7 CATALYTIC ACTIVITY OF PALLADIUM SUPPORTED ON MEISOPOROUS METAL OXIDES IN LOW TEMPERATURE MTHANOL DECOMPOSITION. M.P. Kapoor, Yasuyuki Minamurra, Wenjie Shen, Osaka National Research Institute, AIST, Ibaraki, Osaka, JAPAN.

Methanol decomposition [CH3OH → H2 + CO; ΔH = 22 kcal mol⁻¹] is applicable for waste heat recovery. Palladium supported on various metal oxides has received considerable attention and is preferable for the low temperature liquid methanol decomposition. In the present work we have investigated mesoporous metal oxides (ZrO2·MS41 and TiO2·MS41) as an active support of palladium catalysts prepared by the deposition-precipitation method, which can provide nano-meter size metal particles and high dispersion with the support. All catalysts were well characterized using XRD, XPS and
BET surface area measurement, and hydrogen adsorption. The gas phase methanol decomposition was performed in a fixed-bed continuous flow reactor operating under atmospheric pressure. The catalyst was reduced with hydrogen for 1h at 300°C. The conversions of methanol decomposition at 160-200°C over 3-10 wt % Pd increased with increasing Pd loading. Compared to Pd/TiO₂-MgO, the Pd/ZrO₂-MgO is found to be an effective catalyst for the methanol decomposition. The catalyst Pd/ZrO₂-MgO produced considerable higher activity than Pd/ZrO₂. The effect of ultrasonic vibration during the deposition precipitation of Pd on the supports enhances further enhances the catalytic activity. The results demonstrate that the methanol decomposition to hydrogen and carbon monoxide over palladium supported mestastructured metal oxides catalysts have considerably enhanced the range of decomposition catalyst family and opened up new opportunities in the field of methanol decomposition.

11:15 AM PG.8
ATOMIC SPECTROSCOPY ANALYSIS OF ELECTRODEPOSITED NONOCRYSTALLINE-Ni ALLOYS. Martina Thavander, Matthias Abraham, Helen Lane, Alfred Cerezo, George Smith, Department of Materials, University of Oxford, Parks Road, Oxford, UNITED KINGDOM.

Nanocrystalline Ni and Ni alloys have been prepared using electrodeposition in nickel sulphate based baths. This produces fully dense material with grain sizes in the range 3-30 nm. The deposits, having a thickness of typically 0.3 mm, were characterized by XRD, TEM, PIXE, micro-hardness and 3D atom probe analysis (3DAP).

The 3DAP technique makes it possible to perform chemical analysis on a near-atomic scale, which is essential for the studies of nanocrystalline materials. Pure Ni and Ni–Fe were deposited using a pulsed voltage, whereas a constant voltage was used for Ni–P. The concentration of Fe and P, respectively, could be controlled in a wide range. Initial attempts to produce Ni–Fe were also undertaken. The impurity levels were found to be lower, typically <0.3 at % in the as-deposited materials.

In the results, there was no significant enrichment of impurities or alloy elements at grain boundaries could be observed. The thermal stability and grain growth behaviour was also investigated. In Ni–P precipitation of Ni–P and P segregation was observed following heat treatment at 700K.

11:30 AM #PG.9
FEATURES OF TRACTION SURFACE AND GRAIN BOUNDARY STRUCTURE OF BORON NITRIDE NANOCOMPONST AND MATERIALS. S. Roslakhe Andriyvskis, Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow Region, RUSSIA.

Fracture surfaces of TiN, TiAlN, Ti(N)N, and (Ti,Al)N nanocomposites and films were investigated by FE-SEM, conventional SEM, and AFM. Two types of fracture connected with homogenous and heterogenous deformation were observed and discussed in detail. Localized inhomogeneous deformation with the formation of shear bands has been fixed in the case of TiB₂ and AlN films with partly columnar or blocklike structure. Homogeneous deformation at nanolaminate test conditions was observed for films with clearly-defined columnar structures such as TiN, TiAlN(Ti,Al)N films. HRTEM images of these films are also demonstrated and nature of their grain boundaries discussed.

SESSION F7: APPLICATIONS AND PROPERTIES OF NANOPHASE AND NANOCOMPOSITES

1:10 P.M. #ETF.1
CATALYTIC BEHAVIOR AND SURFACE CHARACTERIZATION STUDY OF Pd SUPPORTED ON NONOCRYSTALLINE CeO₂. G. B. Holland, Department of Chemical Engineering, University of Florida, Gainesville, FL; Horst Hain, Thing Films Division, Materials Science Department, Darmstadt University of Technology, Darmstadt, GERMANY.

Catalytic methane oxidation over polycrystalline and nanocrystalline CeO₂-supported Pd/pCeO₂ and Pd/nCeO₂ has been studied using activity and surface characterization experiments. While the untreated CeO₂ supports give 100% methanol conversion at 120°C, the untreated CeO₂ support exhibits little activity for the reaction conditions used. A Pd loading of 5 wt % increases the activity of Pd/pCeO₂ to 50% conversion at 260°C. The best catalyst examined was 40 wt % Pd/nCeO₂ yielding a 50% conversion at 201°C and a 100% conversion below 300°C. The activity of 40 wt % Pd/nCeO₂ does not decrease during 100 hours of exposure to methanol and O₂ at 240°C.

Electrochemical spectroscopy (XPS) and ion beam spectroscopy (IBS) were used to characterize the surfaces of bare supports and catalysts before and after exposure to reaction conditions. The XPS results reveal that the Pd surface concentration is an order of magnitude higher for 5 wt % Pd/nCeO₂ than for 5 wt % Pd/pCeO₂ due to the increased surface area of the nanosupport.

Higher CeO₂/Pd ratios were observed for both supports than have been previously for Pd on CeO₂ or CeO₂. Accumulation of CeO₂ on the surface during reaction is significant for the palladium catalyst but not for the Pd/nCeO₂ catalyst. As the Pd loading on Pd/nCeO₂ is increased, the Ce/III/Ce/IV ratio also increases. The surface analysis data are consistent with a precursor-based mechanism in which dissociative methane chemisorption results in a surface methoxy species, which undergoes dehydrogenation to yield hydroxyl groups and a reactive C species. Oxidation of this C species, which is an adsorbed carbonyl, which decomposes to CO₂ product, which the hydroxyl groups can combine with via hydrogenation to form a hydroxymethyl or hydrogenation to form a hydroxymethyl derivative of hydroxymethane.

2:00 PM ETF.2
SOLAR CELL CONTACTS USING NANO-SIZED DISPERSIONS. Doug Schulz, Jason Underwood, Calvin Curtin, Dave Ginkley, National Renewable Energy Lab, Golden, CO.

We have been investigating the use of nanosized particle-based contacts for both CdTe and Si solar cell technologies. The primary motivation has been the development of synthetic approaches to writeable inks leading to ohmic and thermodynamically stable contacts. The ability to tune the contact properties by adjusting the processing temperature is highly desirable in a wide variety of energy conversion applications.

In the area of contacts to CdTe, particles of Hg₃Te₆ and Si had been used as contacts to CdTe/GIS/SiO₂ heterostructures prepared by the standard NREL protocol. First, Hg₃Te₆ and Si were prepared by a metal-melt reaction. After CdO₃ treatment and NP etch of the CdTe layer, particle contacts were applied. The Hg₃Te₆ contacts exhibited good electrical characteristics, with Voc >810 mV and efficiencies >11.5% for most cells. Although Voc >800 mV were observed for the Si contacts, inefficiencies were observed in these devices were limited to 9.1%. Using a large series resistance (>20 ohm) was observed in all samples. In order to explore contacts to Si, we have employed powders of Al and Ag. These samples were first characterized by transmission electron microscopy (TEM), TEM element analysis, X-ray spectroscopy (TEM-EELS), and TEM electron diffraction (TEM-ED).

Next, Al and Ag particles were slurried and tested as contacts to p- and n-type silicon wafers, respectively. Linear current-voltage (I-V) was observed for Ag on n-type Si, indicative of an ohmic contact, whereas the Al on p-type Si sample was non-ideal. A wet-chemical surface treatment performed on one Al sample and TEM-EELS indicated a substantial decrease in the O contaminant level. The treated Al samples showed I-V LV after annealing, which will present preliminary results for inks deposition of contacts to Si.

2:15 PM ETF.3
COLLOIDAL MICROWAVE PROCESSING (CMP) FOR POLYMER FUEL CELL AND PHOTOVOLTAIC APPLICATIONS. Monika Willett-Porcil, Christian Gerk and Tim Schubert, University Bayreuth, Faculty of Applied Natural Sciences, Dept of Materials Processing, Bayreuth, GERMANY.

Synthesis and processing of nanocomposites materials with a high degree of micro- and nanoscale organization is particularly versatile by implementation of non conventional processing conditions and microwave radiation, to a ceramic- or a metal-precursor distributed within a matrix, such as to form a colloid, an emulsion or a co-polymer. In particular, microwave processing of precursor compounds within a self-assembled matrix is of high technical importance for electrochemically and photochemically active materials, e.g., nanocasted oxides, noble metals as well as carbides and nitrides of the Group IV-VI elements (Ti to W). Application of selective microwave heating enables the generation of the catalyst and the electric conductor within a MEA of a polymer fuel cell, preserving the microscale organization of the top layer of the membrane. Similar results obtained on photocatalytically active materials show the influence of the nucleation step of the precursor pyrolysis reaction will be presented, based on experiments on artificial mixed dielectrics. The potential of colloidal microwave processing for nucleation control and for nano- as well as microsized organo-inorganic nanocomposites will be discussed, in comparison to thermal equilibrium conditions, with respect to the catalytic and photochemical properties
of nano-Pt and nano-TiO_2 dispersed within proton exchanging membranes or thermoplastic polymers. The microstructure of the products is characterized by low XPS SEM and by Confocal Laser Microscopy.

2:30 PM F7.4 CONTROLLING NANOSCALE MATTER AND NANOSCALE PORE ARCHITECTURES FOR MANGANESE DIOXIDE
BATTERY MATERIALS: Jeffrey W. Long, Karen E. Sider, Rhonda M. Stroud, and Debra R. Rubiner, Surface Chemistry and Surface Modification Branches, Naval Research Laboratory, Washington, DC.

Aerogels, which are nanoscale mesoporous solids, have been shown to be excellent high surface area, sinter-resistant supports for catalysis. These attributes, when coupled to the excellent mass transport of molecular reactants and products to and from the nanoscale domains of the aerogel through the mesoporous structure, are also equally desirable for electrode materials and electroanalysis. Our prior small-angle neutron scattering studies with aerogels have shown that aerogels with ~85% porosity can be re-wetted without discernable collapse of the aerogel structure. This allows liquid-phase catalysis and electrolysis to be pursued with aerogels, modified aerogels, or aerogel composites. We have explored manganese oxide (MnOx) as a cathode material for battery applications, including batteries based on lithium insertion and the familiar Zn/MnOx alkaline chemistry. Lithium insertion to create mixed-valent MnOx/IV/IX/Ox is often accompanied by irreversible structural changes that can limit the recharging capabilities of the resulting batteries. We have prepared MnOx aerogels, an aerogel, and aerogels using sol-gel chemistry based on the reduction of permanganate by an organic reducing agent in aqueous solution. With appropriate reaction conditions, monolithic MnOx gel can be obtained in which the size of both the nanoscale MnOx domains and the porous network is varied, as characterized by multiple structural and chemical techniques. The electrochemical properties (volumetric and galvanostatic discharge) and charge reversibility of these MnOx materials as aerogels, an aerogel, and aerogel will be described with respect to their Li-ion capacities.

2:45 PM F7.5 GRAIN-SIZE DEPENDENT THERMAL CONDUCTIVITY OF NANOCRYSTALLINE YTTRIA-STABILIZED ZIRCONIA AND DIAMOND COMPOSITES: J.J. Eastman, S. Stoyan, L.J. Thompson, G. Auricchio, K.L. Merkle, Materials Science Division, Argonne National Laboratory, J.J. DiMelfi, Reactor Engineering Division, Argonne National Laboratory, J.P. Singh, Energy Technology Division, Argonne National Laboratory, Argonne, IL.

Nanocrystalline coatings are theoretically predicted to exhibit reduced thermal conductivity compared with the conductivity of their coarse-grained or single-crystal counterparts when the grain size of the coating is reduced below the bulk phonon mean-free-path-length. Yttria-stabilized zirconia (YSZ) thin films with grain sizes as small as 2.5 nm or as large as single crystals are being produced by metal-organic chemical vapor deposition (MOCVD). The thermal conductivity of these coatings is being measured using the 3-omega technique. Approach of a factor of 2 in thermal conductivity is seen at ambient temperature for the smallest-grained coatings compared to the conductivity of coarse-grained or single crystal coatings. Biomass disk-and-tube tests are being carried out on MOCVD-produced coated samples prepared under similar conditions to determine if reduced improvements in durability and fracture resistance accompany grain size reduction. A combination of lower thermal conductivity and improved mechanical behavior would make nanocrystalline coatings excellent candidates for future applications as thermal barriers. Measurements of the thermal and mechanical behavior of commercial YSZ thermal barrier coatings using the same techniques will also be described and discussed. In contrast to low thermal conductivity of YSZ, diamond is well known to exhibit extremely high thermal conductivity. This, combined with excellent mechanical and tribological behavior, makes nanocrystalline diamond coatings potential candidates for a number of future applications including, for example, in mechanical systems (MEMS). Thermal conductivity measurements using the 3-omega technique are being carried out on diamond films prepared by chemical vapor deposition. Implications for potential future uses of diamond coatings will be discussed. This work is supported by the U.S. Department of Energy, BES-DM5, under Contract W-31-109-Eng-38 and by grants from Argonne Coordinating Council for Science and Technology.

3:30 PM F7.6 CAN WE DETERMINE THE BARRIER RESISTANCE FOR ELECTRON TRANSPORT IN LIGAND STABILIZED NANOCRYSTALLINE ALUMINA COATINGS FROM INTEGRAL CONDUCTANCE MEASUREMENTS? U. Simon, University of Essen, Institute for Inorganic Chemistry, Essen, GERMANY.

The small lateral size of chemically tailored ligand stabilized metal and semiconductor nanoparticles in the range of one to two nanometers leads to a ultra-small self capacitance in the order of $10^{-12}$ F. This enhances the charging energy essentially above $k_B T$ even at room temperature, which make them interesting as building blocks for nanoscale microelectronic devices, like single electron transistors.

By means of integral temperature dependent conductance measurements, the effective capacitance $C_{eff}$ of the particles in two or three dimensional ligand stabilized nanoparticles is produced from the activation energy $E_A$ of the charge transport according to $E_A \cdot C_{eff}$ [2]. Determining the barrier resistance $R_b$ of the insulating ligand from the overall resistance falls, since the resistance is very sensitive towards disorder, which cannot be avoided in this size scale, by nature.

In this work the use of the Landauer formula [3] is proposed to deduce $R_b$ from $E_A$, when it is taken as the barrier height. According to this, the barrier resistance in ligand stabilized nanoparticles, connected by spacer molecules to form networks [4] depends exponentially on the inter particle spacing. Comparison with data of the single molecule resistance of different ligands determined by local probe techniques, like scanning tunneling spectroscopy, shows remarkable correspondence. This shows that the method proposed is suitable to deduce single molecule properties on the nanoscale from integral measurements.


3:45 PM F7.7 PHYSICAL AND MECHANICAL PROPERTIES OF CO-Cr COATINGS FOR APPLICATIONS AS ORTHOPEDIC IMPLANTS: D. Cheng, M.L. Liu, E.J. Laverne, Department of Chemical and Biochemical Engineering and Materials Science, University of California, Irvine, Irvine, CA; J.C. Laverne, Department of Orthopedics and Biomedical Engineering, University of Miami, Miami, FL.

Conventional and nanocrystalline Co-Cr (ASTM F75) coatings were prepared by high velocity oxy-fuel (HVOF) thermal spraying. The adhesion of the coatings to the Ti substrate was tested by tensile test and microhardness and modulus of coatings were measured using a nano-indentor. The corrosion resistance was characterized by in vitro potentiodynamic anodic polarization technique in a pseudo physiological solution. Both coatings show excellent adhesion strength while the nanocrystalline one has higher hardness and higher corrosion resistance, showing better application potential for orthopedic implants.

4:00 PM F7.8 NANOPOROUS ALUMINA COATINGS FOR MEDICAL IMPLANT AND STENTS - RADIOTHERAPY, DRUG DELIVERY, BIOLOGICAL COMPATIBILITY. Wolfgang Brandau, Alfons Fischer, Guenter Schmid, Thomas Sawicki.

A new method for engineering the surface - body - interaction occurring with implant material by applying a nanoporous coating is presented. This coating is made of nanoporous alumina, formed by nanodispersion of alumina plasma coated implants. By a simple electrochemical process pores perpendicular to the implant surface are formed, whose diameter is adjusted by the anodic potential and can be varied between 5 and 250 nm. By varying the thickness of the coating this technique can be scaled to different loadings of drug carriers. The coating can be used for radiotherapy, drug delivery and biological compatibility as well. After chemical modification of this coating applied to an intramascular stent it is possible to find various radioactive isotopes irreversibly into the inner pore wall which allows for effective radiotherapy. The effect of porosity and chemical modification on the stability of the binding of 90m-Tc to the implant surface is presented as well as first results on cell culture tests proving the biological activity of the radioactive nanoporous ceramic coating.

4:15 PM F7.9 SITE SPECIFIC SELF-ASSEMBLY OF Si/SiO_2 NANOPARTICLES USING PATTERNED PMDS/SIO_2 FILMS: Thomas S. Phelan-Bobin, Richard J. Muehlen, Rote Papadamitsopoulos, and Jeffrey T. Koberstein, Department of Chemistry, Polymer Science Program, Nanomaterials Optoelectronics Laboratory, Institute of Materials Science, University of Connecticut, Storrs, CT.

The present paper discusses the site-specific selfassembly of Si/SiO_2.
n nanoparticle, which provides the means for the formation of three-dimensional supramolecular structures. Ultrathin films of poly(dimethylsiloxane) (PDMS) were typically patterned with exposure to ozone assisted ultraviolet (254 nm) conversion of PDMS to hydroxyl-free SiO$_2$ surfaces. Preferential deposition of SiO$_2$ coated Si nanoparticle, with average size of 20 nm and size distribution of about 25% onto uncovered PDMS surfaces rather than the oxidized hydroxyl-free SiO$_2$ surfaces enables a novel fabrication methodology of spatiotemporally patterned nanocomposites. These nanocomposites were characterized with an array of analytical techniques in order to provide insight into the unique properties of this new class of material. The coverage achieved by this method shows potential for use in numerous applications in the photonics area, particularly when it is incorporated with nano-scraping techniques.

**4:30 PM F7.10 Abstract Withdrawn.**

**4:45 PM F7.11 ELECTRICAL PROPERTIES OF NONCRYSTALLINE TUNGSTEN TITRIOXIDE. A. Heel, L.B. Kiss, R. Vajtai, G. Nikolaou, C.G. Granqvist, E. Olson, Department of Materials Science, Uppsala University, SWEDEN.**

Tungsten oxide is a material of significant interest for applications in several areas. It can, for example, be used as the absorbing material in solar cells or as the electrode material in smart windows. Tungsten trioxide nanoparticle was used in an advanced gas evaporation unit where the tungsten oxide was oxidized in low pressure ambient air. The tungsten trioxide particles were formed via vacuum condensation and coated with oxygen by gas deposition technique to avoid agglomeration effects. The average size of the primary particles was around 5 nm depending on the heating power and the pressure. The particles exhibited a body centred cubic structure. The impedance spectrum showed resonance peaks and negligible admittance effects. The behavior was compared to the behavior of films produced by sputtering techniques. The correlation between fabrication conditions, structure and impedance spectrum will be discussed.

**SESSION F8. POSTER SESSION: NANO-HASEL/SYNTHESIS, CHARACTERIZATION, AND PROPERTIES Chair: Horst Hahn, Seidai Komoreni and John C. Parker Wednesday Evening, December 1, 1999 8:00 P.M. Exhibition Hall D (H)**

**F8.1 MICROSTRUCTURE AND MECHANICAL PROPERTIES OF OXIDE ELECTRODE FIBERS**

Stephen D. Darbin, Akira Yoshikawa, Kenji Hasegawa, Jong-Ho Lee, Boris M. Egelsbaai, Taungo Fukuda, Tokohu University, Institute for Materials Science, Sendai, JAPAN; Yoshikawa Wako, Japan Ultra-High-Temperature Materials Research Center, Ube, JAPAN.

Directionally solidified oxide electrodes have attracted much attention as structural materials because of their exceptional mechanical properties at high temperature [1]. To date, we have focused our attention on sapphire/YAG and refined composites sapphire/Ba-Al$_2$O$_3$, where Y is replaced by a rare earth R = Gd, Dy, Ho, or Er. We have used the micro-pulling-down technique [2] to grow eutectic fibers over a wide range of growth rates, from 0.015 to 28 mm/min. The strength of these materials is strongly dependent on their microstructure, which varies with both composition and pulling speed. The microstructure of this type, in which the two phases form a complex, continuous, interpenetrating network. The interface between domains, as studied by transmission electron microscopy, is atomically sharp. Especially for thin fibers, the mechanical properties, in addition to the oxidation and corrosion resistance, depend on the nature of the surface. We have used atomic force microscopy to characterize both the surface and the bulk microstructure of the fibers. The script microstructure extends to the surface, but there it differs from the bulk in both composition and domain size, exhibiting a larger surface oxidation and smaller domains. The surface tends to approach the bulk properties as the growth rate increases. To better understand and control these characteristics, we employed the computer model to simulate the eutectic solidification process, which yields insight into formation of the Chinese script microstructure [1]. Y. Waku, N. Nakagawa, T. Wkllahoro, H. Ota, K. Shimizu, and Y. Koto, Nature 389 (1997) 49 [2]. A. Yoshikawa, B. M. Egelsbaai, T. Fukuda, K. Suzuki, and Y. Waku, Jpn. J. Appl. Phys. 38 (1999) L55.

**F8.2 INSULATOR-METAL TRANSITION IN NANOstructured NiAl THIN FILMS. Ho-Ping Ng, Alfonso H.W. Ngan, The Univ. of Hong Kong, Dept of Mechanical Engineering, Hong Kong, P.R. CHINA.**

The electrical resistance of Ni-Al alloy thin films prepared by dc magnetron sputtering was found to be absolutely high at room temperature. However, when heated to elevated temperatures, the resistance dropped significantly, exhibiting a remarkable negative temperature coefficient of resistance (TCR). The phenomenon was found to be substrate independent. Cross-sectional transmission electron microscopy revealed that the films were essentially particulate and porous in nature. Although quantum-mechanical tunnelling is generally regarded as the dominating transport mechanism in porous films, our results seem to suggest that localized charged carriers ejected by thermionic emission mechanisms are probably the effective conduction sources in our Ni-Al films at elevated temperatures. Analysis of the current density-electric field (J-E) characteristics yielded a satisfactory agreement with the space charge limited (SCL) and the Poole-Frenkel (PF) emission models, indicating an emission-based conduction process rather than tunnelling in the films. The negative TCR effect diminishes and the usual metallic resistance is restored in thicker films, probably due to reduction in particle separation and coalescence of neighbouring crystallites.

**F8.3 RAMAN SHIFT AND BROADENING IN STRESS MINIMIZED GE NANOCRYSTALS IN SILICON OXIDE MATRIX. Yinciong Jie, Alfred Huan, Andrews Wee, Zhe Xiang Shen, Dept of Physics, National Univ of Singapore, Kent Ridge, Singapore, SINGAPORE.**

Ge$_2$Sb$_2$O$_7$, alloy films have been synthesized by co-sputtering Ge and Sb targets using an rf-magnetron sputtering machine. By intentionally lengthening the cooling time interval in the annealing process and reducing the cooling gradient in the samples, the resulting Ge nanocrystals embedded in amorphous silicon oxide matrix have been found to be nearly spherical, well-dispersed in the matrix and nearly stress-free by means of XRD, HRTEM, EDX and temperature-dependent Raman scattering characterization. Significant Raman shifts ranging from 2.0 to 5.8 cm$^{-1}$ have been observed from samples annealed at different temperatures. A phonon confinement model with various weighting functions and dispersion relations have been used to fit room temperature Raman spectra from selected samples. The size-dependent shift and broadening is found to be in good agreement with Foschetti's phonon confinement model together with the isotropically TO$_3$ phonon dispersion relation introduced by Sussk et al. The Raman spectra can also be well-fitted using peaks calculated from the phonon confinement model without any artificial treatment. The inhomogeneous Raman peak broadening from samples annealed at lower temperatures were attributed to the non-Gaussian size distribution of Ge nanocrystals. The irregular compressive stress reported in the literature may originate from Ge nanocrystals surface strain formed during a fast cooling process due to the mismatch of thermal expansion coefficients of the matrix and the Ge nanocrystals.

**F8.4 SYNTHESIS AND CHARACTERIZATION TWO NOVEL COBALT VANADIUM OXIDES AS CATHODES IN LITHIUM BATTERIES. Fan Zhang, Peter Zawalij and M. Stanley Whittingham Materials Research Center and Chemistry Department State University of New York at Binghamton, Binghamton, NY.**

There has been much interest in the last two decades in layered vanadium oxides and their intercalates because of their potential use as secondary cathode materials for advanced lithium batteries. Therefore, the already rich chemistry of the vanadates compared to layered metal oxides is well established. With open framework was considerably replenished with many new structures. We report here two novel cobalt vanadium oxides, [Ni(CH$_3)$_2]_2[Co$_3$(VO$_7$)$_2$] and [Co$_3$(VO$_7$)$_2$]. The two compounds were synthesized by the hydrothermal reactions of vanadium (V) pentoxide, CoSO$_4$ or Co(COOH)$_2$, with an organic templating cation, tetramethyl ammonium hydroxide or trimethyl ammonium hydroxide at 170$^\circ$C for 72 hours. The stoichiometry, phase and structure of the compounds have been examined as a function of deposition conditions using XRD, DCP, TGA, FTR, SEM and EDX. In these double sheet oxides, organic species do not appear to impede the incorporation of lithium. They readily react with lithium solutions. Galvanostatic cycling of different electrodes based on these compounds revealed a high charge capacity and promising cyclability. Electrochemical properties and rate capabilities of the materials used as cathodes for lithium cells will be presented. Supported by the National Science Foundation.

**F8.5 Abstract Withdrawn.**
FS.6
NOVEL SYNTHESIS OF II-VI SEMICONDUCTOR NANOCRYSTALS. Gregory A. Khitrov, Geoffrey F. Strouse, University of California Santa Barbara, Department of Chemistry, Santa Barbara, CA.

A long-standing goal in materials chemistry has been the synthesis of high quality II-VI semiconductor nanocrystals by wet chemical methods. Currently, the best nanocrystals are produced by solvothermal methods that require the use of organometallic precursors, which are expensive and cumbersome to handle under controlled atmosphere. We present an alternative crystal seeding method using molecular precursors. The growth of nanocrystals from the precursors can in most cases be carried out at lower temperatures than used in solvothermal technology. Results of characterization by electronic absorption and emission spectroscopy, TEM, EDS, and ICP-AES will be presented.

FS.7
ENCAPSULATION OF NANO PARTICLES IN CROSSLINKED RESORCINARENE 'SKINS'. Stephen V. Patrascu, Shouhong Zou, Alexander Wei, Dept. of Chemistry; Kevin B. Stevens, Ronald P. Andres, Dept. of Chemical Engineering, Purdue University, West Lafayette, IN.

Neutral nanoparticles are metastable and require organic surfactants to prevent their irreversible aggregation in solution. This approach, however, has only been successful in stabilizing particles of a limited size range. We have developed a novel encapsulating procedure for stabilizing nanoparticles using resorcinarenes as surfactants, which can then be crosslinked to form permanent-like colloidal dispersions. This organic 'skin' imparts remarkably stability to the nanoparticles, allowing them to withstand a wide range of chemical processes while retaining their dispersity in organic solvents. This has also allowed us to isolate the particles and to characterize them as discrete chemical entities. Characterization of these encapsulated nanoparticles includes GPC-HPLC, TEM and surface-enhanced Raman spectroscopy. Our resorcinarene-based system is able to stabilize neutral gold nanoparticles of at least 20 nm in diameter, and promises to be of general utility. The improved processability of the encapsulated nanoparticles should be useful for their directed self-assembly into arrays and other periodic structures for the development of nanoelectronic networks.

FS.8
STRUCTURE AND STABILITY OF NANO-SCALE PHASES IN MgO-CaZn-Alloys. P.M. Jardim and L.G. Soleriano, PUC-Rio de Janeiro, J.B. Vander Sande, MIT, Cambridge, MA. W.W. Park, KIMM, Kyungnam, KOREA.

Alloys, with six different compositions in the system Mg-Ca-Zn in the form of ribbons with approximately 70 µm thick and 3mm wide, were produced by melt spinning under argon using a CuBe wheel with a speed of 30-50 m/s. These alloys were analyzed by means of Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Energy Dispersive Spectrometry (EDS). The phase stability is being studied by Differential Scanning Calorimetry. To correlate the structural and mechanical properties, the ribbons are being tested by micro-indentation. TEM and field emission SEM have been proved to be essential tools to fully characterize the microstructure. The first technique, however, has demanded particulate sample preparation procedure in order to obtain electron-transparent foils free of artifacts induced by electrolyte contamination. The combination of this procedure with dimpling polishing and ion-milling cleaning is described in the presentation. The result microstructure is presented as based on nanostructured (and, perhaps, amorphous) matrix containing a rather copious population of precipitates mainly based on CaZn and Ca2Mg2Zn13. All the six compositions have shown a microstructural gradient from the wheel contact side to the argon nozzle atmosphere side as a result of the differences in the solidification rate across the ribbons. Work is being planned in the direction of incorporating rare earth additions into the system. The phase stability and the microstructural evolution will be discussed based upon TEM and FEI-SEM observations.

FS.9
SILICON NANOPARTICLE FORMATION BY LASER ABLATION IN A LOW PRESSURE INERT GAS. Naoko Kudo, Satoko Kano, Takafumi Seto, AIST-MITI, Mechanical Engineering Laboratory, Tsukuba, JAPAN; Takehiko Yoshida, Mie University Research Institute Tokyo, Inc., Kawasaki, JAPAN; Nagarnj R. Rao, MicroTherm, LLC, Minneapolis, MN; Steven L. Girishk, Univ. of Minnesota, Dept. of Mechanical Engineering, Minneapolis, MN.

Laser ablation is a promising method for the synthesis of nanocrystalline particles of a wide range of sizes with no contamination. We have produced 1-30 nm-diameter silicon particles by laser irradiation on a substrate in 1-20 Torr inert gas. It was found that the size, shape and structure of particles depend on the experimental conditions of laser irradiation and ambient gas. The size of primary particles or nanocrystalline grains, which is important for the expected application of Si nanoparticles for luminescence devices, increases as the ambient gas pressure is increased, and can be controlled by the pressure. Simultaneously published studies of particle generation using the classical theory of droplet formation in an expansion plume could not explain the experimental observations, e.g., the above-mentioned pressure-dependence of the particle size and also the reported observation of the clusters in the mass spectrum. We have described the clustering of silicon vapor with high kinetic energy and the evolution of particles in the free-molecule regime by a model which considers the effects of induced surface waves and three-body recombination, and which uses a simplified expression for the temperature and density change in the plasma with time. A comparison with the experimental results is shown and the validity of our approach is discussed.

FS.10
ATOMIC SCALE STUDY OF Pt NANOC LUSTERS ON TiO2 (110). Shupan Guo, Yong Ling and Ronald R. Boer, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA.

Understanding the interaction of titanium dioxide with its supporting metal is important to photocatalytic applications. TiO2 (110) has two surface phases: (1x1) and (1x2). We have conducted a comparative study on the interaction of Pt with these two phases using scanning tunneling microscopy/spectroscopy (STM/STS), x-ray photoelectron spectroscopy (XPS), and low energy electron diffraction (LEED). It has been found that Pt forms nanoclusters on TiO2 surfaces. On the (1x1) structure, Pt clusters randomly distribute on the surface at 300 K. In contrast, Pt preferentially adsorbs on the (1x2) reconstruction. Atomic resolution STM images reveal that these clusters are attached to bright spots at the end of atomic rows, with a mean size of 40 Å in diameter, and are 2.4 Å higher than the surrounding atomic rows at the Pt coverage of one monolayer. The electronic information of these clusters is examined by bias dependent images and scanning tunneling spectra. Further annealing of the surface to 450 K causes coalescence of some clusters. By the means of statistically analyzing STM images, the size distribution of Pt clusters is obtained as well as the diffusion length of Pt on TiO2 surfaces, which will be further discussed at the meeting.

FS.11
LOW DOSE HREM IMAGING OF SMALL ANGLE GRAIN BOUNDARIES AND DISLOCATIONS IN DCDH POLYDIACETYLENE NANOCRYSTALS. Christian Koeble, Lawrence Drummond, and David C. Martin, The University of Michigan, Materials Science and Engineering, Ann Arbor, MI.

We have been examining the influence of specific grain boundary and dislocation defects on the microstructure and macroscopic properties of semiconducting, conjugated crystalline polymers. Low Dose HREM has been used to image the internal structure of DCDH polydiacetylene nanocrystals prepared by hydrothermal reaction from dijodination into water. HREM images of several different crystallographic zones have been obtained with reflections in the FFT observed cut to scattering vectors corresponding to a resolution of 0.19 nm. The lattice images reveal the internal perfection of the DCDH polymer nanocrystals, and provide evidence for dislocations, small angle grain boundaries, and lattice bending. Digital FFT's of the HREM images were used to obtain quantitative maps of the size and extent of the local structural variances. The beam stability of the organic DCDH nanocrystals was sufficient to facilitate the acquisition of a series of HREM images as a function of objective lens defocus.

FS.12
SYNTHESIS OF NANOstructured TUNGSTEN CARBIDE FILMS BY LASER ABlation OF MICROPARTICLE AEROSOLS. Michael P. Beem, Michael F. Becker, James R. Brock, Dale E. Henshaw, John W. Ketel, Gokul Mallyahmanth, William T. Nicholas, University of Texas at Austin, Dept. of Physics, Austin, TX.

Tungsten carbide (WC) coatings are prepared using a novel process, pulsed laser ablation of microparticle aerosol. The produced nanostructures are superimposedly impacted onto glass, silicon wafers and stainless steel substrates. The influence of experimental parameters (laser fluency, pressure, number of shots) on the structure, composition and physical properties of the resultant particle and films are studied. It was found that stoichiometric, crystalline films could be grown at rates of nearly 1 micron per second using a wide variety of processing conditions. These films pass both the adhesive lift off and scratch tests. TEM investigations indicate that the laser ablation forms individual particles (2-10 nm) and small...
aggregates of these particles. Adjustment of the gas pressure in the laser interaction cell was found to control the degree of agglomeration while laser fluence and focal position on nanoparticle target during airless impact, the separate particles form dense, self-sintering nanocrystalline films, with helium forming the most dense as determined from SEM images. However, at the high impaction velocities of helium, particle bounce off from the substrate occurred. An increase in the supersonic nozzle diameter was found to reduce this problem and increase deposition rates. This work was supported by the NSF (grant no. CTS 9215371), the Texas Advanced Technology Program (grant no. 3699-348) the Robert A. Welch Foundation and by an MRS Undergraduate Materials Research Initiative grant.

FS. 13
PREPARATION AND PROPERTIES OF COLLOIDERAL PARTICLES. SILICA ON YTTRIUM IRON GARNET.
R.H. M. Gole, M. Jafelici, Jr., Joaquim Portillo*, Sao Paulo State University Chemistry Institute, Campus de Araruama, BRAZIL and
*Seccia Clinto Tecnicos, University of Barcelona, Barcelona, SPAIN
Various properties of particles can be altered by coating them with a layer of different chemical composition. Specifically, yttrium iron garnet (YIG) has been coated with silica particles for the control of their sintering, corrosion resistance, and stabilization of magnetic properties. This cover was obtained by hydrolysis of tetramethylorthosilicate (TEOS) in 2-propanol. This material was characterized by transmission (TEM) electron microscopy, (XEDS) X-ray energy-dispersive spectrometry, (XPS) X-ray photoemission spectroscopy and (VSM) vibrating sample magnetometry. YIG was heterocoagulated and binded by TEOS. The electron diffraction patterns for YIG and silica were obtained and the elements detected by XEDS. XPS measurements indicated that only binding energy for silicon and oxygen were found, on the silica shell, which confirmed that YIG was covered. The values of the saturation magnetization differ from the heterocoagulated system to well-crystallized YIG.

FS. 14
OPTICAL CHARACTERIZATION OF A SPHEROIDAL NANOPARTICLE ON A SUBSTRATE. Carlos E. Roman-Velazquez, Cecilia Noguera and Ruben G. Barrera Instituto de Fisica, Universidad Nacional Autonoma de Mexico, Mexico DF, MEXICO
We developed a spectral representation for the effective polarizability of a spheroidal nanoparticle located at an arbitrary distance above a substrate. This representation allows systematic studies of the optical response of the system in terms of the excitations of optical modes, including multipolar contributions. As an example of its applicability, we study the optical response of potassium particles with different anisotropies, located at different distances above substrates of different materials (Si, TiO2). We present results in terms of differential reflectance spectra that allow us for direct comparison with experimental measurements.

FS. 15
Abstract Withdrawn.

FS. 16
NANOCRYSTALLINE THICK FILMS BY CHEMICAL VAPOR SYNTHESIS. S. Scalfied, M. Winterer, H. Hahn, Darmstadt University of Technology, Department of Materials Science, Thin Films Division, Darmstadt, GERMANY.
Crystalline ceramic films with thicknesses up to 150 microns and grain sizes below 30 nm are prepared by a modified Chemical Vapour Deposition (CVD) method, the Chemical Vapor Synthesis (CVS) on different substrate materials. A horizontal hot wall reactor is used for the pyrolysis of metalorganic precursors under helium flow using various precursor delivery techniques. The influence of process parameters on the grain size, orientation and density of the films is investigated. The influence of process parameters on the symbol reactor position on the microstructure and phase evolution is examined. One dimensional growths in concentrations and porosity are obtained by variation of parameters during the process.

FS. 17
ON THE INFLUENCE OF SOME SYNTHESIS TECHNIQUES ON THE LOW TEMPERATURE SUPERPLASTIC DEFORMATION BEHAVIOUR OF NANOCRYSTALLINE ZIRCONIA. U. Betz, S. Rhee1, S.S. Bhattacharya2, N.S. Gajbhiye3 and H. Hahn, Department of Materials Science, Thin Films Division Darmstadt University of Technology, Darmstadt, GERMANY; 1Department of Technical Physics, Materials Science Division, Research Centre, Karlsruhe, GERMANY, 2Permanent Address: Department of Metallurgical Engineering, IIT Madras, Chennai, INDIA, 3Department of Solid State Chemistry, IIT Kharagpur, INDIA.
It is now well established that nanocrystalline yttria stabilised zirconia is capable of exhibiting superplastic deformation in tension and compression at relatively lower temperatures (less than half the aluminia melting point) (in overlapping transformation temperature range). In this study, nanocrystalline powder produced by several methods of synthesis: (a) two vapour phase condensation techniques, an Inert Gas Condensation (IGC) and a Chemical Vapour Synthesis (CVS) process, (b) a sol-gel method and (c) a laser ablation technique (produced through a corolla technique) has been used. In the case of the IGC process, nanocrystalline zirconia was separately synthesised and subsequently stabilised by physically mixing with the required quantity of nano yttria (lactic produced by this IGC process), whereas in the other three processes nano yttria stabilised zirconia was directly synthesised by in-situ doping of yttrin in zirconia. The powders synthesised from these different processes were separately consolidated and compacted to a green density of about 50%. A standardised sintering route was chosen for an optimal combination of high density and fine grain size (well within the nanometric range). The green compacts were sintered essentially in vacuum at 1423K with a holding time of 120 mins. The sintered specimens were then tested under compression for their deformation behaviour at a temperature of 1423 K. The difference in the low temperature superplastic deformation behaviour of the different powders is expressed in terms of some of the phenomenological constants of high temperature deformation. Microstructural characterisation was also carried out at each and every stage with a view to highlight the differences in the powders produced from the different synthesis techniques.

FS. 18
ARC DISCHARGE FOR THE SYNTHESIS OF MONOCLINIC GaN, NANOWIRES. Young Chul Choi, Dong Jee Bae, Seung Mi Lee, Young Soo Park, Young Bee Lee, Dept. of Semiconductor Science and Technology and Semiconductor Physics Research Center, Chonbuk Natl Univ, Cheonju, R.O.KOREA; Kyeong-Su Park, Analytical Engineering Laboratory, Samsung Advanced Institute of Technology, Suwon, R.O.KOREA; Min Bong Choi, Nae Sung Lee, Jong Min Kim, Display Laboratory, Samsung Advanced Institute of Technology, Suwon, R.O.KOREA.
Monoclinic gallium oxide (β-Ga2O3) nanowires were catalytically synthesized by electric arc discharge of GaN powders mixed with a small amount (less than 5%) of Ni and Co [1:1] under a pressure of 500 Torr [80%Ar + 20%O2]. Scanning electron microscope (SEM) and transmission electron microscope (TEM) images showed that the average diameter of the wires were about 30 nm and their lengths were as long as up to a few hundreds micrometers, resulting in extremely large aspect ratio. Selected area electron diffraction pattern was indicative of single crystalline nature of the β-Ga2O3 wire. High resolution TEM showed twin defects and jog dislocations. Some metal particles are enclosed within the wires. Both X-ray diffraction (XRD) powder and Raman spectra of the wires identified the growth of GaN nanowires as monoclinic crystalline gallium oxides. Growth mechanism in conjunction with catalytic step growth will be further presented.

FS. 19
SYNTHESIS OF CUBIC AND RHomboHEDRAL PHASED NANOCRYSTALLINE SnO2 DOPED In2O3 ITO POWDERS WITH COPRECIPITATION METHOD. Bong-Chull Kim, Jong-Joo Kim, Kyung-sup Nael Univ, Dept of Nanometric Materials Engineering, Tongji, KOREA; S-Hong Chung, KETI, PyungTae, KOREA.
Nanocrystalline SnO2 doped In2O3 [ITO] powders were prepared by coprecipitation from homogeneous solutions and then calcination of these precipitates. Characteristics of precipitates were investigated with the controlling of coprecipitation conditions (pH, concentration of solution, and aging temperature, etc.). When the coprecipitation procedure was carried out with high pH, concentrated solution, and aging temperature, the structure of precipitates was indium hydroxide [In(OH)3] with rod-like shape. On the contrary, indium oxide hydroxide [InOOH] with globular shape was formed in low pH, diluted solution, and high aging temperature condition. Furthermore, when the indium hydroxide [In(OH)3] and the indium oxide hydroxide [InOOH] were calcined at 600°C, each precipitates were transformed to the cubic and the rhombohedral ITO phase, respectively. Besides, the size and shapes of powders were preserved after calcination process.

FS. 20
SYNTHESIS, CHARACTERIZATION, AND UTILIZATION OF SINGLE CRYSTALLINE NANOPARTICLES OF SILVER. Ziyi Zhang, Yadong Yin, Byron Gates, Yongan Xig University of Washington, Department of Chemistry, Seattle, WA.
We have demonstrated the use of Tollens’ reaction in generating
monodispersed, single crystalline particles of silver with diameters in the range of 2-60 nm. The nucleation and growth of these nanoparticles was monitored using UV-Vis spectroscopy and transmission electron microscopy (TEM). Upon exposure to nm-metallic molecules, the plasmon peak of these silver nanoparticles changed substantially in intensity and/or position. The potential use of this optical property in fabricating new types of optical sensors will be discussed.

**FS 21**

**SI NANOPARTICLES SYNTHESIZED BY BALL-MILLING A MIXTURE OF GRAPHITE AND SI DIOXIDE POWDERS. C. Lamm, Y.F. Zhang, Y.H. Tang, C.S. Lee, I. Bello, S.T. Lee, Centre of Super-Diameter and Advanced Films and Department of Physics and Materials Science, City University of Hong Kong, HONG KONG.**

Since Cahn has reported intense visible photoluminescence (PL) from porous Si at room temperature, light emission from Si nanostructures has given rise to enormous interest in view of the potential applications in photonic devices. Mechanical activation by ball-milling is a popular method to make nanocrystalline materials because of its simplicity, the relatively inexpensive equipment, and applicability to essentially all classes of materials. However, normal mechanical milling technique produces Si nanostructures not by cluster assembly but by the structure decomposition. The sizes of the produced Si nanoparticles are normally too large to exhibit quantum confinement effects. Recently, we found that ultrafine Si nanoparticles can be synthesized by solid phase reaction of graphite and Si dioxide powders in ball-milling processes. The generated Si in solid phase assembled as nanoparticles in a wide spectrum of diameters. Intense multiple-peak structures in the photoluminescence spectra of the Si nanoparticles were observed at room temperature. The peak energies are found to coincide well with the photoluminescence peak pinning energies previously reported in porous Si. Thus the fine structures of luminescence spectra can be attributed to the size quantization of Si nanoparticles formed during solid phase reaction processes of ball milling. In this paper, both the synthesis of Si nanoparticles by ball milling from mixtures of graphite and Si dioxide powders and the PL characteristics are presented.

**FS 22**

**PREPARATION OF NANOCRYSTALLINE BISMUTH-CONTAINING POWDERS THROUGH SOLUTION-PHASE REDUCTIONS. Edward E. Bao, Alan D. Berry, Arthur W. Snow, and J. Paul Armstead, Naval Research Laboratory, Chemistry Division, Washington, DC.**

Current studies into the chemical synthesis of suitable metal nanoparticles have focused primarily on the d-block elements, with little work examining the preparation of similar materials from the main group metals. Recently, in an attempt to both synthesize such materials and understand the fundamental chemistry behind their formation, we have begun to examine the preparation of nanocrystalline bismuth and bismuth/gold alloys through several straight-forward solution methods. Nanocrystalline bismuth powders with approximate average particle sizes ranging from 15 to 30 nm have been prepared from the reduction of BiCl₃. In addition, nanocrystalline Au₃Bi powders of comparable dimensions have been obtained from the reduction of BiCl₃ and HCl (HCl/BiCl₃) precursor, utilizing a phase-transfer reagent. Full details of the synthesis of these materials as well as their characterization through XRD and TEM will be presented.

**FS 23**

**MAGNETIC HARDENING OF MECHANICALLY ALLOYED SmFe₁₋ₓCoxTi₃. Lotfi Benattia and Catherine Djega-Mariadassou, CNRS, LCMTR, Thiers, FRANCE.**

Mechanical alloying of ternary SmFe₁₋ₓCoxTi₃ (x = 0, 0.5, 1, 1.5, 2) alloys was carried out under an Ar atmosphere, milled samples were annealed for 30 min in a vacuum at different temperatures Tₓ from 650°C to 1150°C. The effect of heat treatment on the structure and magnetic properties were investigated by means of X-ray diffraction (refined using the Rietveld method), Mössbauer spectroscopy and differential sample magnetometer. Tetragonal Tb₂Fe₁₅-type structure is observed for samples with x<0.6. After 900°C (Curie temperature Tₓ for x = 1, as an example). For 650Tₓ＞850°C the TbCu₂-type phase was identified as the unique phase (Tₓ = 327°C for x = 0.5). Between these two regions a mixture of Tb₂Cu₁₁ and Tb₁₂Fe₁₅-type nanocrystalline phases is obtained with a maximum of the coercive field Hc (Hc > 5 kOe) and of the energy product (BH)max. The Mössbauer spectra relative to the hexagonal phase show sextuplets broadened by the statistical occupancies of the iron sites. The relationship between the magnetic behaviour and the lattice parameters of the trigonal and the tetragonal phases can be deduced. The experiments with annealing temperature variation were repeated for all composition of alloys. An enhancement of the magnetic properties results from the Co substitution.

**FS 24**

**ORDERING IN NANOCRYSTALLINE SmFe₃. Catherine Djega-Mariadassou and Lotfi Benattia, CNRS, LCMTR, Thiers, FRANCE.**

Three samples of nominal atomic Sm composition consistent respectively with the stoichiometric 1/12, 2/17 and 1/7 were prepared by high energy ball milling of Fe and Sm mixed powders and subsequent annealing at temperature Tₓ between 873 and 1423 K. The X-ray analysis by the Rietveld method, taking into account diffraction domain size and strain effects was coupled to Curie temperature Tₓ measurements and the Mössbauer spectral refinement at room temperature. For all samples, at Tₓ between 873 and 1023K, the detected out-of-equilibrium phase is the hexagonal P6₃/mmm structure derived from the TbCu₂ phase with the composition SmFe₃. The increase of the 2Fe atomic site occupation favors the Tb₂Fe₃ phase for Tₓ>973K, the Tb₃Fe₃ phase at 1273K to the 12Fe/3 Sm/217 structure. The Mössbauer experimental spectra of the samples annealed at Tₓ = 1273K, are similar to earlier works devoted to Sm₃Fe₁₅. The spectra assigned to SmFe₃ are explained by one hyperfine field field close to the 2Fe dumbbell close to the value observed for the 4Fe₃ phase. The two remaining hyperfine fields broadened by a quadrupole split distribution are assigned to the two remaining Fe families. They are increased comparatively to the values shown by the derived atom families of Sm₃Fe₁₅, inducing a higher Tₓ for the SmFe₃ phase. For intermediate Tₓ, the reduction of the broadening is centered on lower field values in accordance, to a better known reduction of the 2Fe dumbbell site. This result is connected, too, to a decrease of Tₓ explaining the wide spread of Tₓ values found in all previous works.

**FS 25**

**SIZE EFFECT IN GERMANIUM NANOSTRUCTURES FABRICATED BY PULSED LASER DEPOSITION. E. Hassen, A.K. Sharma and J. Narayan, Department of Materials Science and Engineering, and NSF Center for Advanced Materials and Smart Structures, North Carolina State University, Raleigh, NC; J.F. Muth, C.W. Tong, and R.M. Kolbas, Department of Electrical and Computer Engineering, North Carolina State University, Raleigh, NC.**

We have fabricated ten alternating layers of Ge nanostuctures buried in AlN and Al₂O₃ matrices grown on Si(111) and sapphire by pulsed laser deposition (PLD) at the substrate temperature of 500°C. The characterization of these structures was performed using high resolution transmission electron microscopy (HRTEM), photoluminescence, Raman spectroscopy and transmission measurements. The HRTEM results show that the Ge islands are single crystal with a pyramidal shape. The average size of Ge islands was in the range 3.5-20 nm for different laser deposition and substrate parameters. The Raman spectrum showed a peak of the Ge-Ge vibrational mode downward shifted up to 295 cm⁻¹ for the 15nm size nanocubes which is quantized confinement of phonons. Photoluminescence of the Ge dots (size 165nm) was blue shifted by -1160 meV from the bulk Ge value of 0.28 eV at 77 K, resulting in a distinct peak at 3.1 eV. The transmission measurements carried out at room temperature and 77K on different samples deposited on n-type substrate showed shift of both E₁ and E₂ transitions in the allowed spectral region for the Ge dots in accordance with the quantum confinement effect. The size effect of Ge nanostuctures on optical properties is discussed and the importance of PLD in fabricating novel nanostuctures is emphasized in this paper. Reference: 1. K.M. Hassen, A.K. Sharma, J. Narayan, J.F. Muth, C.W. Tong and R.M. Kolbas, Appl. Phys. Lett. (in press 1999)

**FS 26**

**CHARACTERIZATION OF INCLUSIONS IN RUTILE NANOPARTICLES. Shirley Turner, Surface and Micronanotechnology Division, Chemical Science and Technology Laboratory, National Institute of Standards and Technology, Gaithersburg, MD.**

The surfaces of rutile (TiO₂) have been the subject of considerable study, in part because rutile can be used as a photocatalyst to disinfect water and organic compounds. Previous work showed that rutile particles (voids), are formed by cleavage at the rutile crystal surface. The particles are observed using transmissive electron microscopy (TEM) and characterized by bright and dark-field imaging, electron diffraction and high-resolution TEM. Inclusions were viewed in many orientations including down rutile [001] and in orientations perpendicular to [001]. The voids are observed voids or cavities formed by the insertion of rutile particles. TheTAB inclusion of the rutile particles have the rutile crystal face (110) faces that are squares with
rounded corners when viewed down [31]. Some of the particles with central inclusions have additional smaller inclusions. Upon heating in the electron beam of the oxidized and polymeric inclusion from facets. Upon further heating, the inclusions have been observed in many cases migrate or change size. Possible factors involved in the morphological changes to the inclusions upon heating will be explored.

**FS. 28**

**THE ROLE OF BORON IN THE MECHANICAL MILLING OF TITANIUM: 50% ALUMINIUM 4% VANADIUM POWDER**


Titanium 60% Aluminium 4% Vanadium (Ti-6Al-4V) is widely used for commercial superalloys forming (SPF) and a reduction in grain size would lead to improved mechanical properties [SPF].

**Mechanical alloying (MA)** of Ti-6Al-4V with a second phase is a possible route to producing a fine-grained, particularized, reinforced material.

Boron is an ideal choice for a second phase because of its combination of the MA and powder the boron will react with the titanium to form stable TiB reinforcing particles. Although boron has a low solid solubility in titanium it is expected that the MA process would at least lead to a nanoscale mixing of boron. Furthermore boron is known to stabilize amorphous structures of alloys. It is therefore of interest to focus on the exact role boron plays in the MA process. The clean mechanical alloying of gas-atomised Ti-6Al-4V with 0, 5, 15 and 50 at 5% is being carried out at the Defence Evaluation Research Agency, UK [1]. The powder samples have been analysed using XRD, thermal analysis and analytical TEM (EDS and PEELS). The nanocrystalline nature of the powders is confirmed and the effect boron has on the evolution of their microstructures will be reported.

**FS. 30**

**SYNTHESIS AND OPTICAL PROPERTIES OF STABLE ORGANIC DISPERSIONS OF BISMUTH SULFIDE NANOPARTICLES**

Datnasti Negashia, Nicholas Kotov, Oklahoma State University, Chemistry Department, Stillwater, OK.

The synthesis of semiconductor nanoparticles with high chalcogen/metal ratio, such as bismuth sulfide, is complicated by the insufficient passivation of their surface when traditional Lewis base stabilizers such as thiol, selenol, phosphines, etc., are utilized. Many of these materials have a long gap in the near IR region, and therefore a strong short quantum effect is expected in the visible region of spectrum provided that the diameter of nanoparticles does not exceed a few nm. Two types of synthetic strategies were utilized to obtain nanocrystals of bismuth sulfides: 1) synthesis in acidic media in the presence of pyridine and 2) decomposition of a precursor in the presence of Sc surface. In both cases, the growth of nanoparticles is expected to be impeded by the reaction of Lewis acid centers of the stabilizer with chalcogen atoms on the particle surface. Produced bismuth sulfide nanoparticles were characterized by TEM, XRD, mass-spectroscopy, ultracentrifugation, and optical spectroscopy. A sharp absorption onset has been observed between 550 and 650 nm depending on the method of synthesis, which is attributed to the variations of particle size. A strong luminescence peak was registered in the near-bandgap region of Bi2S3 nanoparticles, when protonated pyridine was used as a stabilizer.

**FS. 31**

**HYSTERESIS LOOP SHIFTS IN MAGNETIC FIELD COOLED FeOOH NANOPARTICLES**

M.S. Sehran and A. Marwan, Physics Department, West Virginia University, Morgantown, WV.

Recently, a number of reports on the structural, catalytic and magnetic properties of commercially available FeOOH nanoparticles have been published [1]. Free-flowing powder can be produced as a single particle size \( \approx 20 \) A, with Fe being in Fe\(^{3+}\) state. Magnetic studies show that this material behaves as a superparamagnetic (SP) with a blocking temperature \( T_B \approx 65 \) K. However the nature of the magnetization below \( T_B \) is not understood and depends strongly on the size of the FeOOH nanoparticles, resulting from the immediate reduction of adsorbed Cu(II) ions. These adsorbed Cu(II) ions create a new energy level in the bandgap of CdS at about 1.2 eV below the conduction band [4]. At higher concentrations of copper(II) ions, ultrasound small particles of copper sulfide are formed on the surface of CdS nanoparticles at the expense of isolated copper ions. Such ultrasound small particles of copper sulfide are non-luminescent, and therefore, the intensity of the new band increases as the concentration of copper(II) ions increases. The formation of ultrasound small particles of copper sulfide can be controlled by using complexed Cu(II) ions instead of free Cu(II) ions [5]. The effect of surface modification of CdS nanoparticles upon its luminescent properties depends upon the amount of adsorbed Cu(II) ions per CdS nanoparticle. An appropriate mechanism will be discussed.


**FS. 32**

**CADMIUM SELENIDE NANOPARTICLES SYNTHESIZED WITH FUNCTIONAL CAPPING GROUPS**

Sebastian J. Nærøe, Paul O'Brien, Department of Chemistry, Imperial College of Science, Technology and Medicine, Exhibition Road, London, UK.

Semiconductor nanoparticles capped with Tri-octylphosphine oxide (TOPO) have been of considerable interest for the past few years. This is because the TOPO route offers narrow size distribution, high degrees...
of crystallinity, colloidal stability over time and robust surface passivation. These characteristics are very important as they directly influence the optical, electronic, and photoluminescent properties of nanoparticles, e.g. quantum yields and deep trap luminescence. Conversely, TOPO causes complications when the nanoparticles are integrated into devices as it is an insulating, wet solid. The conventional approach has therefore been to use the nanoparticles in TOPO and then to replace the capping group by a more labile compound, often a liquid at room temperature, such as pyridine or thiol. However, there are drawbacks to this approach, as the particles are less stable after replacing the capping group by thiol and in the loss of qualities mentioned above. In this work we present CdS nanoparticles synthesized directly in capping agents such as pyridine, thiol and water, and mixtures of these and Trietylphosphine (TOP) or TOPO. Optical measurements such as UV and photoluminescence have been carried out. The particles have been characterized by X-Ray diffraction, Energy Dispersive X-ray Analysis (High Resolution) Transmission Electron Microscopy imaging. Emphasis has also been put on surface functionalization for specific uses during synthesis, so the particles can be reacted with surfaces or self-assemble straight after.

FS.33 SYNTHESIS OF SELF CAPPED METAL SULFIDE NANOPARTICLES. Michael R. Lawell, P. O'Brien, Department of Chemistry, Imperial College of Science, Technology and Medicine, London, UK.

Here we report the synthesis of self capped (where the precursor contains the capping agent) metal sulfide nanoparticles by thermal decomposition in dynamic vacuum, of the novel asymmetric metal dithiocarbamates, 6-bis(N-methylthioethylthiocarbamato)cadmium(II), and zinc(II) [M(S2CN(CH3)2)(CH3CN)] [M = Cd and Zn]. The Cd sulfide dots are cubic in phase when synthesized at temperatures of between 150 and 250 °C. However, when the temperature is increased to 300 °C there is a change in phase of the nanocrystalline CdS, from cubic to hexagonal, as evidenced in the powder XRD patterns. The nanoparticles were soluble in pyridine and photoluminescence with a slight Stokes shift which decreases as the synthesis temperature increases, approaching that of bulk band edge luminescence. The capping group is believed to be the amine [N(C6H4)2].

FS.34 OPTICAL PROPERTIES OF NANOCRYSTALLINE SILICON FILMS WITH DIFFERENT DEPOSITION TEMPERATURE. A. M. Ali, T. Inakuma, Y. Kurata and S. Hasegawa, Kanazawa Univ, Dept of Electronics, Kanazawa, JAPAN.

In these last years, a renewed interest for the growth of nanocrystalline Silicon (nc-Si) which has been demonstrated to have good properties for application in both passive and active electronic and optoelectronic devices. In our previous study [1], PECVD poly-Si films were prepared using SiH4(mercaptomethane) and photoluminescence, PL) of PECVD poly-Si films with different Td (500-700°C) were investigated. The SiH4 and H2 flow-rates were 1.0 and 3.0 sccm, respectively, the film thickness were kept constant 0.2 µm by adjusting the deposition time. The rf power and gas pressure during film deposition were maintained at 20 W and 0.15 Torr respectively. Results showed the E0 characteristic bands were around 1.75 eV at 600-650°C which agree well with the data for amorphous silicon, a-Si, but at Td between 650 and 700°C the E0 characteristic bands strongly increased around 2.1 eV due to small grains included in the film. Therefore, we have shown that the transition from amorphous to nanocrystalline easily occurs at Td of around 700°C using SiH4:H2 mixture. [1] S. Hasegawa et al., J. Appl. Phys. 85 (1999) 3844.

FS.35 INFLUENCE OF DOPING ELEMENTS ON THE SINTERING AND MICROSTRUCTURE OF NANO ALUMINA. Dem Assiantier, CEA, Monts, FRANCE.

The final aim of this work is to correlate microstructural properties and electrical breakdown capability of doped nanosized alumina. Main structural parameters studied are densities, porosities, grain size and shapes, dopants concentrations, volatilization and localisation. Powders were synthesized through sol-gel methods, such as sols precipitation, alcohols hydrolysis-condensation, peptisation. Seeding with alpha alumina has been used in order to promote the phase transformations which lead to these doped bulk phases. Doping (M) was introduced in the form of nitrates. Samples were cold isostatically pressed at 400 MPa and sintered in air around 1500 Celsius degrees. They were analyzed using X Ray diffraction, scanning electron microscopy, electron microprobe analysis in order to determine phases, grain sizes and morphologies and to control dopants repartition. Chromium is uniformly soluble in the alumina matrix. Manganese precipitates in a spinel form. Isothermal and constant rate of heating density were performed in order to determine the part of the neck growth stage, for pure and doped aluminas. The two types of experiments provide complementary results. Chromium inhibits sintering while manganese increases densification. Pure alumina initial sintering is controlled by grain boundary diffusion of alumina. Study of dopants influence on alumina sintering is disturbed by chemical reactions.

FS.36 INORGANIC FULLERENE-LIKE MATERIALS AND NANOBUBBLES (IF) FROM LAYERED COMPOUNDS. Reuven Temne, Yishai Feinman, Gittery, Elia Zvi, Moshe Honyconyn, Weizmann Inst, Rehovot, ISRAEL.

Using the paradigm of carbon fullerenes, it was shown by Temne and co-workers that nanoclusters of layered compounds, like MoS2, are unstable in the planar form and fold into hollow cage structures of various shapes: from spherical and polyhedral to monosomes of a mm length and cross-section of 15-20 nm diameter (IF). Following this discovery a few methodologies for the systematic synthesis of large amounts of IF were pursued. Recently, IF structures from various other layered compounds were synthesized. Interkalation of IF MoS2 rendered these nanomaterials as stable suspensions in organic solvents and photoelectrochemical cells were subsequently prepared. Recently, the first MoS2 octahedra having 572 Mo atoms, were reported. The structural, optical, electrochemical, and tribological properties of IF MoS2 were investigated in some detail. It was found by Feinman et al. that IF MoS2 are semiconductors with a tunable bandgap which scales with the size of the nanoparticles. The 2H polytype structure is locally preserved in these nanoparticles. Few extra Raman lines observed in the IF suggest a reduced symmetry compared with the bulk (2H) predecessor. The tribological properties of IF was shown by Rappaport et al. to outperform the ubiquitous solid lubricants 2H-WS2. This suggests a large range of applications for these nanomaterials. Other applications will be briefly discussed.


Nanoparticles of CdS and Mo-doped CdS capped with TOPO (tris-octylphosphine oxide) and close to nano-dispersed have been prepared by a single source using (methyltrithiolethiono)cadmium(II) and manganese dichloride as a precursor. The nanoparticles obtained show quantum size effects in their optical spectra without the presence of the metal leak through the crystal structure of CdS. Clear difference in photoluminescence results between CdS and CdS:Mo samples ESR spectra and ICP results confirm the presence of Mo in CdS quantum dots. The Selected Area Electron Diffraction (SAED), X-ray diffraction (XRD) pattern and Transmission Electron Microscopy (TEM) show the material to be of the hexagonal phase. The crystallinity of the material was also evident from High Resolution Transmission Electron Microscopy (HRTEM) which gave well-defined images of nanomolecules with clear lattice fringes.

FS.38 ELECTRICAL AND MAGNETIC PROPERTIES OF NANOGRAIN THIN LAYERS FOMED BY MEtal IMPLANTATION INTO SILICON. S. Peng, W.Y. Cheung, M.F. Chiah, C.P. Li, K.Y. Lui, The Chinese University of Hong Kong, Department of Electronic Engineering, Shatin, N.T., Hong Kong, CHINA.

Various kinds of nanograin thin layers were formed by high dose metal ion implantation into silicon using a metal vacuum arc ion source. Characterization of these thin layers was performed using Rutherford backscattering spectrometry, transmission electron microscopy, and electrical measurements. The ion species used included Carbon and Ti and the granulat grain layers consist of nanometer size crystalline metal silicide precipitates embedded in the Si substrate. It was found that these nanograin thin layers exhibit interesting electrical and magnetic resistivity properties. For example, when prepared at appropriate ion implant doses, the C and Ti implanted samples show a nearly temperature-independent electrical resistance from 20K to 300K. Some of the Fe implanted samples exhibit a large positive
magnetoresistance at temperatures lower than about 50K. A magnetoresistance larger than 70% was observed for one sample at 34K. The temperature dependence of the electrical resistance and the magnetoresistance of these samples, and their variation with the processing conditions will be presented and discussed in conjunction with the results of other characterization techniques. This work is supported in part by the Research Grants Council of Hong Kong (Ref. No. CUHK 374/98E).

OPTICAL AND ELECTRICAL CHARACTERIZATION OF A SYSTEM OF [110] ORIENTED SILICON NANOCRYSTALS FORMED BY EXCIMER LASER PULSES IN Si: H FMR ON GLASS. D. Efremova, N. V. Aslanov, V. V. Vasilyev, O. K. Shabanov, S. A. Kodzhab, I. L. Fedina, Institute of Semiconductor Physics SB RAS, Novosibirsk, RUSSIA; V. V. Bologov, Institute of Sensor Microelectronics SB RAS, Omsk, RUSSIA.

The optical and electrical studies of undoped and phosphorus doped a-Si:H films with silicon nanocrystals of various concentrations and sizes formed by excimer laser amorphization (ELAs) were carried out. The band gap of a-Si:H can reach 1.8 eV, band gap for crystal silicon is 1.16 eV, so, electrons can be localized in nanocrystallites. Peculiarities connected with localized electron states within nanocrystals may be expected especially in the case of high concentration of nanocrystals, when a-Si barriers become tunnel thin. The average size (from 2 up to 10 nm) and concentration of nanocrystals were evaluated from Raman scattering and HRTEM data. Due to the presence of nanocrystals the dark conductivity becomes 2-3 orders of magnitude greater. The temperature near 260K the sharp changes of the activation energy from 0.75 to 0.13 eV were observed in the case of a-Si films with 2 nm silicon nanocrystallites. Anisotropy of Raman scattering intensity in different geometries versus angle between polarization vector of incident light and an axis lying in a sample plane was experimentally discovered in system of Si nanocrystals in a-Si:H films. This effect can be interpreted as result of preferred (110) orientation and correlation of in-plane orientation of the nanocrystallites formed by pulse ELAs. Appearance of the preferred (110) orientation in the case of excimer laser amorphization of a-Si:H/ glass structures was supported using HRTEM. It was calculated that the modulation of the temperatures in different scattering geometries versus the above mentioned angle depends on part of self-oriented nanocrystallites. According to Raman data it can be proposed that the part of [110] oriented nanocrystal was 90%, and the part of self-oriented nanocrystals was 3.3%. Deformation mechanism of the observed selforganization of nanocrystals is proposed.

CHEMICAL REACTIONS ON THE SURFACE OF SnO2 NANOCRYSTAL POWDERS. M. Thomas, J. L. Luchow, University of California at Santa Barbara, Santa Barbara, CA

The increase in demand for environment monitoring calls for gas sensors capable of detecting pollutants at sub-ppm levels. Such high sensitivity can be reached by using nanostructured powders in the fabrication of chemical gas sensors. The benefits of using nanopowders are: First, their high surface-to-volume ratio leads to a larger area exposed to the gases to be detected. Secondly, the grain size of the nanopowders becomes comparable to the depth of the depletion layer. It is therefore expected that the sensitivity should be influenced by the particle size.

Besides, it has been proved that nanocrystalline SnO2-based sensors have a maximum sensitivity toward CO at two different temperatures, one of them being close to the room temperature. To clearly understand the CO detection mechanism, the chemical reactions taking place at the surface of SnO2-based sensors have to be studied in close connection with the electrical conductivity variations. These surface chemical reactions inducing the sensor response have been demonstrated to be identical on the real sensor and on the original nanopowder constituting the sensing layer. A very relevant and convenient tool for this dual analysis of SnO2 nanopowders is the Fourier transform infrared (FTIR) spectrometry which allows the in situ investigation of the surface chemical species modifications under various environments, simultaneously with the measurement of the infrared energy transmitted by the sample directly related to the variations of the electrical conductivity.

In this paper, we present the FTIR study of two SnO2 powders with different average grain sizes (13 and 8 nm). The formation of new chemical species at the SnO2 surface subjected to CO at different temperatures is described and the role played by oxygen in the CO detection mechanism is discussed. This work has been partly supported by the European Commission under the BRITTEURAM III program (HPR-CT95-0009).

POLYMERIC EVALUATIONS FROM SILICA SURFACES USING THE RUTHENIUM ALKYLEDENES FROM T. A. M. Thomas, A. P. Seery, Department of Chemistry, Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, CT.

Modification of silica surfaces with rationally designed microstructures is important from both a scientific and a technological point of view. Polymers initiated from the surface allow us to grow layers of polymers directly from the substrate to be modified. One approach to Surface Initiated Polymerization (SIP) is to use surface coupling agents to provide an initiator ligand for a transition metal catalyst. Ruthenium alkylidenes that catalyze ring-opening metathesis polymerizations have been used to generate a variety of functionalized polymer layers in our laboratories. Layers synthesized by this method can incorporate a wide range of functional groups and may be easily modified to provide both hydrophilic and hydrophobic surfaces. Characterization of surface polymerized layers must be performed on two levels. Chemical characterization is performed using IR and NMR spectroscopy. The physical structure of these materials is of interest and we have employed TEM and thermal analysis as well as light scattering to study them.

MASS SPECTROMETRY ANALYZING NANOMATERIALS. A. M. McIver, J. A. Green, G. F. Strouse, University of California at Santa Barbara, Santa Barbara, CA.

Efforts in metal chalcogenide nano-material science at the 1-3 nm scale has opened new routes into materials that exhibit quantized physical properties. These materials can be synthesized as near-zero-disperse with controlled surface capping via hydrothermal methods. Analysis of the structure and molecular-level interactions in these materials is typically center on thin film techniques operating with TEM, X-ray diffraction, UV/Visible, and photoluminescence techniques. These methods are excellent tools for analysis of an ensemble, however they do not specifically address the distribution in compositions and structure. We have developed methodology for exploring particle size and composition utilizing mass spectrometry. ESMs and MALDI ionization methods allow for the direct analysis of mixtures and solved molecules without substantial fragmentation induced by either the ionization method. The analysis of positive and negative ion modes offers a unique opportunity to probe the fragmentation with direct observation of the parent ion in pseudo-positive mode. Correlation of MALDI and ESMs methods provides substantial insight into composition, sample homogeneity, and thermodynamic stability. Analysis of these results provides insight into the applicability of ESMs methods to structure analysis, composition and stability of metal chalcogenide nano semiconductor materials at the 1-3 nm size regime. We have carried out a careful mass-spectrometric analysis on a series of mono-disperse metal-chalcogenide clusters in which the substitution of chlorine and surface are carefully controlled. Analysis of the optical properties with respect to the structure of the cluster suggest the importance of surface derivatization on the lowest optical properties and electronic gap in these materials.

ULTRASONIC FORCE MICROSCOPIC CHARACTERIZATION OF NANOSIZED COPPER PARTICLES. E. J. Schumaker, L. Sun, M. J. Reddick, Shanghai Microstructural Diagnostics, University of Dayton Research Institute, Dayton, OH; Terry Murray, Research Institute and Graduate Materials Engineering, University of Dayton, Dayton, OH.

Ultrasonic Force Microscopy (UFM) has been developed by modifying a Scanning Probe Microscope. Two function generators are employed to drive a piezoelectric transducer in a continuous wave (CW) mode or an amplitude modulated wave (AM) mode. The output is connected to the piezoelectric transducer. The transducer is attached to the back side of the sample. The elastic wave propagating through the sample is detected by an atomic force microscopy tip. Two lock-in amplifiers are then used to measure the magnitude and phase of this elastic wave. In the CW mode, the tip is always in contact with the specimen during scanning. Images of ultrasonic properties can be simultaneously obtained with the topography images. The technique has been utilized to characterize nanoscale copper grains and copper nanoparticles deposited on a quartz substrate by ion beam deposition. Images of the same region obtained with atomic force microscopy (AFM mode) and UFM mode were correlated to be useful. The images reveal how the ultrasonic force microscopy is compared to the origin of image contrast in ultrasonic force microscopy and its utilization for quantitative elastic property measurement of nanometer regions of the material are discussed.

SURFACE ENHANCED RAMAN SPECTROSCOPY, A TOOL TO
INVESTIGATE ULTRATHIN FILMS AND NANOSTRUCTURES ON SURFACES. Giuseppe Campagnini, Dipartimento di Chimica, Università di Roma 'Tor Vergata', Italy.

Surface Enhanced Raman Scattering (SERS) is a promising technique to study the vibrational properties of nanostructures and ultrathin films onto suitable substrates. In fact, this technique makes it possible to study the dependence of SERS enhancement on the size and shape of the sample. In this work, we present some contributions to the understanding of SERS and its application to the investigation of ultrathin films.

In particular, using metal self-assembled monolayers (SAMs) of different length it is possible to study the distance dependence of SERS enhancement as a function of the size of the sample. Moreover, in the study of other molecules with the Enhanced Raman technique, all SAMs can be used as spacer to avoid the direct metal adsorption on the substrate, giving a better understanding of the interaction mechanisms.

Surface Enhanced Raman Scattering (SERS) is a powerful tool for studying the vibrational properties of molecules on surfaces. In this work, we present some contributions to the understanding of SERS and its application to the investigation of ultrathin films.

P.8.45

MICROSTRUCTURAL AND MAGNETIC PROPERTIES OF GRAPHITICALLY ENCAPSULATED Ni NANOCRYSTALS AND PURE Ni NANOPIERCLES WITH NO LAYER. Xiangzhong Sun and M. Jose Garcia. Instituto Nacional de Investigaciones Nucleares (ININ), Mexico.

Graphitically encapsulated Ni nanoparticles [Ni(C)] and pure Ni nanoparticles [Ni(O)] were synthesized via modified arc-discharge method in a methane and a mixture of H2 and Ar. The Ni/C and Ni/O clusters were characterized using electron microscopy, X-ray photoelectron spectroscopy (XPS), and thermal analysis. The results show that the encapsulation of Ni nanoparticles with graphite layers increases their magnetic and metallicity properties.

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P.8.46

TRANSPORT AND MAGNETIC CHARACTERISTICS OF MONODISPERSIVE Co/CoO CLUSTER ASSEMBLIES. Kenji Samejima, Dong Liang Peng, Takashi Hikita, Saei Yamamoto and Yoshiko K. Komeda. University of Tokyo, Tokyo, Japan.

We have fabricated Co-covered monodisperse Co cluster assemblies with the mean cluster size of 13 nm at various oxygen gas flow rates, RO, by a plasma condensation technique cluster beam deposition method. We studied their electrical resistivity, magnetoresistance, and magnetization between 5 and 300 K. For 5 = 0.45 SCCM of the As of the resistivity reveals a minimum and shows logarithmic dependence at lower temperatures, probably due to the local Anderson localization of conduction electrons in disordered oxide shells. A critical temperature of the cluster of 10 K was observed for negative magnetization in this regime.

For 5 > 0.45 SCCM, tunneling type temperature dependence of conductance is observed for the tunneling model. This form of the model is, in fact, a function of the tunneling conductance. The tunneling conductance is observed for 5 > 0.45 SCCM. The tunneling conductance is observed for 5 > 0.45 SCCM.

P.8.47

SPUTTERING EFFECTS AND 2 DIMENSIONAL ARRANGEMENT OF NANOPARTICLES IN INSULATORS UNDER HIGH FLUX Cu IMPLANTATION. N. Kishimoto, C. G. Lee, National Research Institute for Metals, Tsukuba, Ibaraki, Japan. V.T. Grishin, Khar'kov State University, Khar'kov, Ukraine.

Applications of heavy ions, sputtering surface charging, and high flux implantation, enable us to conduct low-energy and high-flux implantation into insulating substrates. Negative ions of 60 keV, at high dose rates, have generated metallic nanocrystals in insulators, suitable for nonlinear optical devices in substrates of amorphous [a-]2 and crystalline[cr-]2 SiO2. The nanocrystals spontaneously grow and eventually lead to a two-dimensional arrangement in a certain dose-rate regime. In this paper, we focus on the effects of surface sputtering on the two-dimensional nanocrystal formation. The Cu-implantation is conducted at high dose rates in SiO2 substrates. The results show that the surface roughness increases, and optical absorption of the plasma peak begins to drop. Coincidentally, the two-dimensional arrangement of nanocrystals occurs, which is a good performance in terms of the projected range of ions. It is a contrast to the cases at the lower dose rates where nanocrystals follow a Gaussian-like profile. The coincidence between the outer and inner processes suggests that the mass transport via the surface influences the nanostructure precipitation of nanocrystals. The results of the nanocrystal statistics and the surface roughness will be presented and the possible correlation will be discussed.

P.8.48

THERMOELECTRIC PROPERTIES OF THE X%Bi2Te3-Y%Sb2Te3 COMPOUNDS BY MA-PULSE DISCHARGE SINTERING PROCESS. Ryo-En Park, Yong-Ho Park, Toshiba, Abe, Materials Engineering Department. National Research Institute for Metals, Tsukuba, Ibaraki, Japan.

The X%Bi2Te3-Y%Sb2Te3 compounds with composition of useful thermoelectric cooling materials were prepared by mechanical alloying (MA) pulse discharge sintering process. Effects of MA times and sintering condition on Seebeck coefficient, electrical resistivity, Hall coefficient, carrier mobility and thermal conductivity of the sintered materials. For typical specimen the temperature dependence of Hall coefficient and carrier mobility were measured over the temperature range from 80 to 350 K and thermal conductivity at room temperature. A thermoelectric characterization of specimens of these p-type compounds is carried out in a function of Seebeck coefficients. The figure of merit Z was found to be about 3.0 × 10^-3 K^-1 for the 25%Bi2Te3-75%Sb2Te3 sintered at 610K using reduced MA powders less than 75 μm.

P.8.49


The electrical resistivity as a function of temperature (4K to 621K) of several electrodeposited nanocrystalline materials [Ni, Ni-Fe, Co] has been examined. The contribution of the grain boundaries to the electrical resistivity was quantified in terms of a specific grain boundary resistivity, which was found to be similar to previously reported values of specific grain boundary resistivity for copper and aluminum obtained from studies involving polycrystalline materials. In the high temperature range, the resistivity of the nanocrystalline samples was measured as a function of time. The observed time dependence of the resistivity at elevated temperatures was correlated to microstructural changes in the material. The study has shown that the electrical resistivity is an excellent characteristic for the study of nanocrystalline materials giving useful information regarding grain size and degree of thermal stress, as well as some insight into the grain growth kinetics at various temperatures.

P.8.50

SIZE DISTRIBUTIONS, OPTICAL PROPERTIES, AND SURFACE CHEMISTRY OF NANOCLUSTERS STUDIED BY LIQUID CHROMATOGRAPHY. D.J. Martin, D.R. Provenco, Nanostructures and Advanced Materials Chemistry Dept, Sandia National Labs, Albuquerque, NM.

We have investigated the cluster size distributions, aging processes, optical properties, and surface chemistry of nanocrystals clusters of Au, Ag, Pt, and MoS2 dispersed in organic solvents using liquid chromatography.
high pressure liquid chromatography (HPLC), dynamic light scattering (DLS), and transmission electron microscopy (TEM). The nanoclusters were synthesized by the hydrothermal reaction at room temperature in inert oil and range in diameter from 1-10 nm. HPLC is used to monitor the changes in cluster size distribution and average cluster size as a function of sample age, surface passivating agent, and metal type. This technique is sensitive enough to discern changes in hydrodynamic volume corresponding to only 2 carbon atoms of the passivating agent or metal core size changes of 3+ and we have determined how the total cluster volume (metal core + passivating organic) changes with passivating agent. At the same time we have measured the optical absorbance properties of these Au and Ag clusters and have demonstrated a significant blue shift in the plasmon absorbance as the Au cluster size is decreased. Remarkably, the smallest Au clusters also exhibit significant visible photoluminescence! It is found that the cluster size distribution in these surfactant-stabilized dispersions is constant with age and this redistribution of cluster mass occurs even in the presence of binding and exchange of the passivating agent. The rate of mass redistribution is most rapid for metals with the lowest bulk melting temperatures (e.g. Au, Ag), and slows for those with the highest melting points (Pt, Pd). It occurs most rapidly with the weakest surface-active agents (polyethers). The narrowing of the cluster size distribution and the preference for certain discrete sizes argue that special structural stabilities overwhelm the expected kinetically-limited Ostwald ripening process historically observed for larger colloids (i.e. >10 nm). We show how HPLC is particularly useful for studying the relative strength of binding of organic molecules to the nanocluster surface-a feature of paramount importance for many applications. This work was supported by the US Department of Energy under contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the US Department of Energy.

**FS 51**

**STEADY-STATE PHASE DIAGRAM OF NANOPHASE**

DEO-MILLED Cu 65 Ag 35 DSC AND ATOM PROBE STUDY.

Bing Wu, Pascal Bellen, Univ of Illinois at Urbana Champaign, Dept of Materials Science and Engineering, Urbana, IL; Allan J. Mydosh, Thomas A. Lushay, Johns Hopkins Univ, Dept of Materials Science and Engineering, Baltimore, MD.

Mechanical alloying is widely used to synthesize nanocrystalline materials. This non-equilibrium processing route induces also compositional phase transformations: in the case of systems with positive heat of mixing, it is often possible to force a solid solution by low temperature milling, or to stabilize a nanocomposite by intermediate temperature milling, due to a fine scale decomposition. In order to gain insight on the fundamental understanding of these driven phase transformations, we have built a diagram of the steady-states reached by Cu-Ag powders milled at temperatures ranging from 80 to 450K, with nominal compositions from 35 to 75% Cu. X-ray diffraction, differential thermal analysis, and atom probe (AP) field ion microscopy are used. At liquid nitrogen temperature, a single solution forms. When ball milled at 450K, two-phase coexistence is observed between a Cu 65 Ag 35 and a Cu 75 Ag 25 solution phases. Above 300K, a coexistence region extends to the equilibrium composition, and close to the equimolar composition, two terminal solid solutions coexist with a solution near the nominal composition. Surprisingly, this two-phase coexistence disappears for compositions away from the equilibrium line, leading only to intermediate phases. We have developed a new method for preparing FIB tips from ball milled powders, which makes it possible to obtain direct atomic scale information on the nanophases described above. Statistical analysis of the data shows in particular that room temperature milling produces a solid solution with short scale and large scale composition fluctuations. The latter inhomogeneities are likely to result from inhomogeneous plastic deformation. At higher milling temperatures, X-ray powder diffraction, transmission electron microscopy, and atom probe data allows measurement of the scale of decomposition as a function of milling temperature. This steady-state phase diagram combined with detailed atomic information should help to select the best possible operating conditions to synthesize, by ball milling, nanocrystalline materials with optimized mechanical or magnetic properties.

**FS 52**

**GLASS FORMATION AND NANOSTRUCTURE DEVELOPMENT IN AL-BASED ALLOYS.**

Robert L. Wu, Gerhard Wilde, John H. Peregudko, University of Wisconsin-Madison, Dept of Materials Science and Engineering, Madison, WI.

Amorphous and nanocrystalline Al-based alloys have attracted much attention for their outstanding mechanical properties such as high tensile strength, excellent fatigue resistance, and corrosion resistance. Al 65 Sn 35 metallic glasses have been produced by rapid solidification processing (melt-spinning) and solid state amorphization (repeated cold rolling).

While the rapidly quenched samples showed a primary crystallization with an exotherm onset around 170°C in DSC and yielded a high density phase change transition at 275°C, the glass transition range, the sample from repeated cold rolling showed a clear glass transition signal at 127°C and no evidence for a primary crystallization. The comparison of these amorphous samples obtained from different reaction pathways suggests that this primary crystallization originates from quenched-in, pre-existing clusters. Moreover, the glass transition temperature (Tg) has been assessed in Al 65 Sn 35 and Al 65 Fe 35 through the application of modulation calorimetry. It has been difficult to measure the glass transition temperature of the amorphous samples that exhibit primary crystallization since the thermal response of the primary crystallization often obscures the observation of the glass transition. The capability of modulating calorimetry to separate heat flow response signals of the reversible and irreversible reactions, the glass transition temperature can be readily measured. In addition, metallic glasses have been incorporated into the Al 65 Fe 35 amorphous matrix during rapid solidification in order to decrease the glass transition temperature. The incorporation of extraneous nucleation catalysts has provided insight into enhancing the glass transition density in amorphous alloys and studying heterogeneous nucleation behavior of nanocrystals in metallic glasses. The support of the ARO (DAAH04-95-1-0261) is gratefully acknowledged.

**FS 53**

**DIRECT TRANSMISSION ELECTRON MICROSCOPY STUDY OF Au-Fs-Au AND GOLD-COATED IRON CORE SHELL NANOPARTICLES SYNTHESIZED USING REVERSE MICELLES.**

W. L. Zhu, E.E. Carpenter, and C.J. O'Connor, Advanced Materials Research Institute, University of New Orleans, LA.

The Au-Fs-Au and gold-coated iron core shell nanoparticles were synthesized using reverse micelles. The core shell structure were observed by transmission electron microscopy (TEM). The X-ray energy dispersive analysis (EDAX) and selected-area diffraction pattern (SADP) also confirmed that the successful synthesis of the core shell structure. The average size of Au-Fs-Au and gold-coated iron were 9 nanometer and 8 nanometers, respectively. Shell structures with different thickness and shape were also observed. The outside shell lattice were easily observed in both nanoparticles. The magnetism of both kinds of nanoparticles were also characterized.

**FS 54**

**FORMATION OF FE-BASED NANOSTRUCTURED ALLOYS BY RAPID SOLIDIFICATION.**

Q. Li, H.W. Kui, The Chinese University of Hong Kong, Dept of Physics, Shatin, N.T., Hong Kong, CHINA.

Recently, it [1, 2] was demonstrated that liquid phase spinodal decomposition can take place in undercooled melt eutectic alloy at low temperature (96°C) [3]. The liquid phase spinodal decomposition involves the formation of two metastable phases, of compositions corresponding to the two eutectic reactions and T: temperature of the undercooled melt. At still higher DT, it turns out that the wavelength of the spinodal network can be less than 100 nm (3). The morphologies of the liquid spinodal network can then be frozen by subsequent solidification of the Fe-C melt. The formation of the nanocrystalline/micronanocrystal material in this study is made to synthesize Fe-based nanostructured alloys. References 1. C.W. Yue and H.W. Kui, J. Mater. Res., 13, 3104 (1998). 2. H.W. Guo, C.C. Leung, and H.W. Kui, J. Mater. Sci., 33, 4829 (1998). 3. H.W. Guo, L.F. Chan, and H.W. Kui, submitted.

**FS 55**

**FEETULAR TEMPERATURE DEPENDENCE OF THE RESISTIVITY OF GAS DEPOSITED NANOCRYSTALLINE GOLD FILMS.**

J. Ederer, L.B. Kins, G.A. Niklinski, C.G. Granqvist and E. Olsson, Dept of Materials Science, Uppsala University, SWEDEN.

Nano-crystalline gold films consisting of high quality particles show interesting properties below 20 K. For small grain size with narrow size distribution the influence of the truncated phonon spectrum yields an exponential decay of the phonon resistivity. For annealed films with larger grain sizes a T 4 dependence is observed, indicating the existence of low angle phonon scattering.

**FS 56**

**CHARACTERIZATION AND SYNTHESIS OF BICONDUCTOR NONPOROUS METALS.**

S. Conner, George Washington University, Dept of Materials Science and Engineering, Blacksburg, VA.

The preferential dissolution of one element in a binary alloy has been used to produce electrodes of nanoporous metal. The porous metal morphology can be thought of as a monophasic material consisting of a bicontinuous network of solid and void phases; both phases have length scales of order 20 nm. These materials have potential as high
surface were ares in such applications as amperometric sensors. Despite the interest in these materials, very little is known about the physical phenomena associated with them. For example, little is known about the effect of the interplay of factors such as the dopant concentration and the various crystallographic aspects of the thin film on the grain boundary location and the conduction mechanisms. The main difficulty in characterizing the phenomena is the fact that the grains are typically very small, on the order of 1 to 2 nm, and it is difficult to observe their structure directly.

FS. 57
PROTEIN SUPPORTED METALLIC NANOSTRUCTURES AS CATALYSTS - Silvia Behrens, Wilhelm Habicht, Nikolos Beukis, Eckhard Dieck, Technische Universität, Osnabrück, Germany. Germany.

There is an increasing interest in nano-sized metal particles due to their new catalytic and electronic properties. With decreasing particle size the ratio of surface to volume increases continuously, so that the particle properties are more influenced by the surface atoms instead of the lattice atoms. The smaller and the more monodisperse the particles are, the better should their catalytic activity. Particles in the nanometer size range reveal a great potential for heterogeneous catalysis. One disadvantage of such particles, however, is a certain tendency to agglomerate and to lose catalytic activity, thus making them difficult to support on a support material.

Highly oriented protein assemblies with characteristic nanometer-sized period patterns are a promising substrate for the growth of metallic nanoparticles. Following a bottom-up approach, noble metal particles in the nanometer size range are obtained by the reduction of the corresponding metal salts in the presence of the protein assemblies. By reduction of an aqueous palladium salt solution, palladium nanoparticles (1-5 nm) could be nucleated and immobilised on the tubulin lattice of microtubules for the growth of gold nanoparticles.

The catalytic activity of the protein-supported particles is determined by hydrogenation reactions.

FS. 58
GRAIN BOUNDARY STRUCTURE IN NiFe NANOCRYSTALS. H. N. Frey, B. Pults, California Institute of Technology, Pasadena, CA; J. L. Robertson, S. Spooner, Oak Ridge National Laboratory, Oak Ridge, TN.

We made small angle neutron scattering (SANS) and Mössbauer spectroscopy measurements on four NiFe materials with an average grain size of 6 nm; nanocrystalline material prepared by mechanical attrition, nanocrystalline material after an exposure of 4 K, nanocrystalline material after temperature treatments of 100°C for 10 days, and a cold sample composed of large crystals. The thermal treatments of the nanocrystalline materials caused changes in the intensity and the slope of the Ln(I) vs. Ln(Q) plot at large Q of both the nuclear and magnetic scattering profiles of the SANS measurements. The Mössbauer spectra of the nanocrystalline samples showed changes in the hyperfine fields associated with grain boundary regions. The changes induced by cryogenic exposure and annealing at 100°C were somewhat different, but both were consistent with a sharper density gradient between the crystalline region and the grain boundary region. Some grain boundary atoms in mechanically attrited NiFe are in high-energy positions, and shift into new positions during low temperature treatments. Since a subset of the unique properties of nanocrystalline materials originates from the high density of grain boundaries present in nanocrystalline materials, grain boundary atomic structure could have a large impact on the transport properties of nanocrystalline materials. Possible evidence of the effects has been seen in previous phonon density of states (DOS) measurements on NiFe nanocrystals. The room temperature phonon DOS of NiFe nanocrystals with an average grain size of 6 nm and a large grain boundary volume fraction of 0.15 as high as 10 kg K^2 cm^2 in the same powder after it had been exposed to 10 kg or 350 kg for 8 hr.

FS. 59
SHAPE-DEPENDENT THERMODYNAMIC PROPERTIES OF NANOCRYSTALS. Z. L. Wang, M. Mhanna, S. Link, J. Petrichki, and M. A. El-Sayed, School of Material Science and Engineering, Georgia Institute of Technology, Atlanta, GA.

The surface selectivity and activities of shape controlled nanocrystals, such as platinum nanocrystals and gold nanorods, strongly depend on their sizes and shapes. Shape effects to the surface selectivity of nanocrystals with controllable shapes [1, 2]. Their thermodynamic properties, such as surface stability, shape transformation and melting behavior, are becoming interesting. The microstructures of the nanoparticles synthesized in the tetradecane and transoctadecane Pt nanoparticles have been studied by in-situ transmission electron microscopy (TEM) [3]. Our results indicate that the surface coverage polymer is removed by increasing the sample to a temperature of 180°C for 4 h, while the particle shape shows no change to -350°C. In a temperature range of 350°C to 450°C, a small transformation occurs in the particle shape but no major shape transformation. The particle shape experiences a dramatic transformation into spherical-like shape when the temperature is higher than ~350°C. The macroscopic melting occurs at ~350°C, much lower than the melting point of bulk Pt (1773°C). Gold nanorods of aspect ratio 3:7 have been synthesized by a reverse microemulsion technique. The thermodynamic property of the Au nanorods is interesting because the nanorods are nearly single (100) and (110) facets. The presence of 110 facets, a high energy surface, is a unique characteristic of Au nanorods. In-situ TEM has revealed the surface diffusion, sublimation, and growth of the nanorods of different sizes, clearly displaying the shape-dependent properties of nanocrystals. T. S. Ahmadi, Z. L. Wang, T. C. Green, A. Henglein and M. A. El-Sayed, Science, 1996; 272, 1994. Z. L. Wang, T. S. Ahmadi and M. A. El-Sayed, Surface Sci., 1997, 380, 302. Z. L. Wang, J. Petrichki, T. Green and M. A. El-Sayed, J. Phys. Chem., 1998, 102, 6145. Research was supported in part by NSF DMR-9733160.

FS. 60
COLD WELDING OF GOLD AND PLATINUM NANOPARTICLES. Seng Lu, Nan Yu, Ilhan A. Akgun, Princeton Materials Institute and Department of Chemical Engineering, Princeton University, Princeton, NJ.

Cold welding (sintering) of nanosized gold and platinum particles has been observed at temperatures below 250°C, but the mechanisms for this phenomena are still not clear. In our study, monodisperse 20 nm Au particles and 2 nm Pt particles were prepared via sodium citrate reduction of appropriate metal salts. The morphological changes of the particles at the contact zone in chemical composition caused by sintering Au-Au or Pt-Pt nanoparticles under electron beam were investigated using transmission electron microscopy (TEM). Complete lattice alignment via atomic-level rearrangement was observed at the completion of the sintering of Au-Au or Pt-Pt particles. In contrast, the frequent recrystallization of lattice was observed during the sintering between Au and Pt particles. A curve-fitting of experimental data on the neck growth of Au particles revealed a linear relationship between the rate of neck growth and the inverse of the neck radius, agreeing with the mass transfer model for plastic deformation. The atomic concentration profiles of Au-Pt binary systems revealed the absence of Pt in the Au phase, but as much as 15% of Au in the Pt phase, contradicting the prediction by conventional binary phase diagram for bulk Au and Pt. This deviation from phase diagram is attributed to the formation of an amorphous Pt phase that accommodated more Au atoms.

FS. 61

Blue-colored aqueous colloids of highly crystalline tin dioxide nanoparticles have been prepared hydrothermally either by doping the nanoparticles with tin- or by introducing oxygen vacancies into the SnO2 lattice. Temperatures above 250°C during the synthesis are required to achieve blue-colored particles in the 4 to 9 nm size range. The blue color corresponds to a broad absorption peak in the red and the near-infrared region. Powders of SnO2 or SnO that exhibit an up to 10 fold increase in electrical conductivity as compared to the corresponding yellowish material obtained by the usual low temperature synthesis. For both, non-conductive yellowish nanoparticles as well as for the SnO2-based red SnO2 the oxidation state and the coordination of tinymuny have been investigated by near edge x-ray absorption fine structure measurements (XANES) at the Sn L-edge and by extended x-ray absorption fine structure measurements (EXAFS) at the Sn K-edge. Based on these measurements, a two-step reaction model for the formation of conductive tinymuny doped tin dioxide is proposed. In the absence of tinymuny, blue-colored colloids of SnO2 nanoparticles are obtained, whereas if the hydrothermal synthesis is performed in reducing atmosphere (and T > 250°C). In this case, the blue color vanishes slowly, if thecolloid is exposed to oxygen.
indicating that oxygen vacancies have been introduced into the lattice during the synthesis. Based on these results, the IR absorption band containing the blue color of the material is assigned to a plasma excitation of free carriers in n-doped nanoparticles. For SnO nanoparticles doped with 6%imony, the peak position of the absorption band indicates an electron density of about $5 \times 10^{20}$ cm$^{-3}$, in agreement with literature values for conduction layers of the corresponding material prepared by sol-gel techniques.


We quantitatively investigated the extreme strengthening of Ni produced by hard-particle dispersions with particle sizes and separations in the nanometer range. Ion implantation of Al and O was used to form cubic phase Al$_2$O$_3$ or NiO at volumes fractions of 10 or 15% with average sizes from 1.5 to 14 nm as observed by TEM. The intrinsic, substrate-independent elastic and plastic mechanical properties of the nanometric alloyed layers were evaluated through nanoindentation testing in conjunction with finite-element modeling. Force-versus-depth data were evaluated using a Mises yield criterion with no work hardening in the precipitated zone, giving the flow stress and Young's elastic modulus. As expected, the influence of the nanoparticles on the elastic modulus was modest, being less than a factor of 1.5. Flow stress was increased far more with values ranging up to 4.0 GPa, as compared to 0.15 GPa for untreated Ni at 92% plastic strain. Our results agree qualitatively with continuum dislocation-hardening theory for dislocation blocking by spherical particles: the experimental flow stresses vary in inverse proportion to particle size as predicted, and the absolute magnitudes of the experimental and predicted flow stresses correlate well, when combined uncertainty, which is about a factor of 1.4. Moreover, when the present findings for Ni are combined with our earlier results for strengthening of Al by Al$_2$O$_3$ nanoparticles, the entire body of experimental information is quantitatively unified by the theory. This study demonstrates that nanoscale strengthening of Ni can be extended to $\cdot$5 GPa, and that such strengthening is described by continuum hardening theory despite particle size and separations of only a few nanometers.


**FS.63** DEFECT CHEMISTRY IN TiO$_2$ AND CeO$_2$ NANOCEAMICRICES. P. Basset, Universite de Provence, Marseille, FRANCE; H. L. Teller, MTT, Cambridge, MA

The electrical and thermodynamic properties of titanium dioxide and cerium dioxide nanoceramics were examined by impedance spectroscopy and electrochemical methods. The data were analyzed with respect to the presence of point defects and dopants with interfaces. The influence of dopant segregation, reduction of defect formation and migration energies, enhanced interfacial diffusion and the existence of metastable phases on properties are discussed. The impact on applications, such as sensors, catalytic activity and oxygen storage capacity of nanoceramics is pointed out.

**FS.64** SOLUTION-BASED SYNTHESIS OF MAGNESIUM OXIDE NANORODS. Qingqiao Wei, Harvard Univ., Dept of Chemistry and Chemical Biology, Cambridge, MA; Charles M. Lieber, Harvard Univ., Dept of Chemistry and Chemical Biology and Div of Engineering and Applied Science, Cambridge, MA

A solution-based synthesis route was developed to produce large quantities of MgO nanorods. Hydrated basic magnesium chloride, which has an amorphous structure, was dehydrated to form a dehydrated MgO nanorod. A subsequent two-step transformation process with magnesium hydroxide as an intermediate product was able to preserve the crystal form of the precursor to yield magnesium oxide nanorods. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) of the MgO nanorods show that the products are very pure (>95%) crystalline MgO nanorods with diameters from 40 nm to 200 nm and lengths 10 microns or longer. High resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) further confirm that the MgO nanorods are single crystalline and that the rod axis is along <110> direction. A model for the structural transformation from hydrated basic magnesium chloride to magnesium oxide has been developed and compared to our experimental results. This solution-based process can be easily scaled-up, and is a low-cost source of pure magnesium oxide nanorods needed in many industrial applications, for example, as reinforcing agents in matrix composites and in flux-pinning centers in high-T$_c$ superconductors.

**FS.65** UNEXPECTED PREPARATION OF NONAPASEIC FLUORIDE III CONDUCTORS. Georges Denes, Delphine Le Roux, M. Cecilia Munich, Alena PerFederal, Jossedal Viged and Shizue Shiu, Cordoba University, Dept of Chemistry and Biochemistry, Laboratory of Solid State Chemistry and Mossbauer Spectroscopy, and Laboratory for Inorganic Materials, Montreal, Quebec, CANADA.

Fluoride ion conductors are materials that exhibit an unusually efficient motion of the fluoride ions over very long distances, well beyond the melting point. These high-temperature oxide fluoride ion conductors have the fluoride type structure (beta-PbF$_2$) or are derived from it by cell distortion and superstructures (Pb$_2$SnF$_4$). Amorphous or nanocrystalline phases are usually obtained either by prolonged milling, for example, or by precipitation, or ultrafiltration from the gaseous or liquid states. We have developed two new procedures that give tin(II) containing fluoride ion conductors that have the fluorite-type structure and are nanocrystalline. In these materials, tin(II) and the other metal (Ca, Sr or Pb) are fully disordered on the (124) site. This is a highly unusual feature, considering the covalency of the SnF$_2$ bond in contrast with the M$^+$ typically ionic bond, and also considering that the tin and M coordinations are highly different. Nanocrystalline cubic gamma Pb$_2$SnF$_4$, M$^+$[x]Sn$_2$[x]F$_2$, and Sn$_2$Pb$_2$F$_7$ and Pb$_2$SnF$_6$ have been obtained by ball-milling and leaching in aqueous solutions. Their preparation and study will be discussed.

**FS.66** EFFECT OF VAPOR PRESSURE OF H$_2$O ON THE FORMATION OF NANO CRYSTALLINE TiO$_2$ ULTRAFINE POWDERS. Kuo-Ren Lee, Sung Jung, Dept of Ceramic Engineering, Yongin, Joo Sung Song, KERI, Changwon; Sun Joo Kim, KAERI, Daejon, ROK (Republic of Korea).

Mono-dispersed TiO$_2$ ultrafine particles with diameters 40-400 nm were obtained from aqueous TiOCl$_2$ solution with 0.67M Ti$^{4+}$ concentration prepared diluting TiCl$_4$ by homogeneous precipitation process in the range of 17-230°C. With the spontaneous hydrolysis of TiCl$_4$, which means the nanosize increase of pH value in the aqueous solution, all mono-dispersed precipitates were crystallized with the anatase or rutile TiO$_2$ phase. TiO$_2$ precipitate with the rutile phase was fully formed at the temperatures above 65°C, not involving the transformation of H$_2$O, and more above 150°C, which were promoted by suppressing it. TiO$_2$ precipitate with rutile phase including a small amount of the anatase phase started to be formed in the intermediate temperatures above 70°C showing the full formation of the anatase above 95°C under the free evaporation of H$_2$O. However, in the case of completely suppressing H$_2$O evaporation at the temperatures above 70°C, TiO$_2$ precipitate with rutile phase was fully transformed with the reaction time into the precipitate with the rutile phase by the vapor pressure of H$_2$O. Therefore, the formation of TiO$_2$ precipitates with the rutile phase around room temperature would be caused due to the existence of the capillary pressure between the agglomerated needle-shaped particles or the ultradisperse clusters, together with the slow reaction rate.

**FS.67** SUPERPARAMAGNETIC FERRITES: REALIZATION AND PHYSICAL OBSTACLES. Dietrich Vollath, Eric Pellegrin, Dorothee V. Schubl, Forschungszentrum Karlsruhe, Karlsruhe, GERMANY.

Superparamagnetic nanocrystalline ferrites have a high potential for application in high frequency systems such as cellular phones. In these materials, the change in the direction of magnetization is not associated with the movement of Bloch walls, but with thermal fluctuation of the magnetization vector. Therefore, the resonance frequency of the Bloch walls, found as frequencies below 200 MHz, is no longer limited the maximum frequency for application. This new limit is given by the frequency of electron spin resonance in the gigahertz range. It was possible to verify this behavior in all ferrite-type ferrites, based on Ca$_2$Fe$_2$O$_4$. Changing the composition of the spinel changes the energy of magnetic anisotropy controlling the susceptibility and the maximum frequency for applications. It was possible to show that the superparamagnetic nanocrystalline ferrites have their frequency limit beyond 2 GHz. In all cases the materials were nanocomposites made of ceramic or polymer coated nanoparticles produced by the microwave plasma process. The coating of the particles is necessary to reduce spin - spin coupling destroying superparamagnetism. Even when the susceptibility is in the range of today's commercial ferrites, the saturation magnetization is always found to be significantly smaller than the theoretically expected value. This phenomenon is a recently discovered property of the X-ray magnetic circular dichroism. These investigations show a significant orbital magnetic moment antiparallel to the direction of the spin moment in these ferrites. These moment thus, according to Hartmann rules, should quake, with the latter moment by the spin moment. Additionally, it was found that the amount of Fe$^{3+}$ ions is
larger than expected by thermodynamic data of bulk materials. Point defects that can be healed out at temperature below 300 °C lead to a further reduction of the magnetization.

**FS.68**

NANOSIZED ALUMINA POWDERS VIA FLAME SPRAY PYROLYSIS: SYNTHESIS, CHARACTERIZATION, AND MICROSTRUCTURAL EVOLUTION.

T.R. Hinkin, R.M. Laine,
University of Michigan, Dept. of Materials Science and Engineering, Ann Arbor, MI.

We recently described methods of producing various nanosized oxide powders by flame spray pyrolysis of novel alkoxide complexes. This scalable synthetic route provides reproducible, high purity, multimetallic nanosized powders. We can currently make single crystal oxide powders (280 nm dia. and surface area of 40-60 m²/g) at production rates in excess of 100 g/hr. The flexibility of the FSP process also allows for the incorporation of dopant atoms into the nanosized powders. This presentation will focus on the effect of several dopants on the formation, sinterability and microstructural evolution of FSP Fe-Alumina powders, 25 nm average particle size.

**FS.69**

SINTERING BEHAVIOR OF NANOSIZED CERAMIC COATINGS.


This paper concentrates on the sintering behavior of nanosized ceramic coatings, e.g. silica and zirconia, produced with the sol-gel-processing route. Because the sintering behavior of the sol-gel coating is a crucial aspect the paper focuses on the microstructural mechanism of sintering of nanosized ceramic coatings. The sintering takes place in a furnace and the results are compared with laser sintering. Especially, attention is paid to the densification behavior and the grain growth in the layer. Also the different crystal phases observed are addressed. Experimentally it was found that a green layer with a maximum thickness of about 350 nm could be attained. At greater thickness the green layer exhibited severe cracking. The samples were examined using ellipsometry and in situ environmental scanning electron microscopy (FEG-SEM-Philips XL30S and FEG-SE-Philips XL30S with a special electromagnetic lens). A high resolution TEM (JEOL 4000/II) was used to study the sol-gel-spherical particles. With ellipsometry layer thickness and density in sol-gel derived zirconia layers could be obtained. Complete densification of the sol-gel-derived coatings was found at temperatures above 1000 °C. The various stages of sintering were explained based on a viscous sintering regime and a crystalline sintering regime.

**FS.70**

MESOSCOPIC SILICA FILMS GROWN AT THE AIR-WATER INTERFACE.

Nam Yoo, Anthony Y. Ke, Horiyuki Nakamura, Tu Lee, Dudley A. Sadcola, Princeton University, Princeton Materials Institute and Department of Chemical Engineering, Princeton, NJ.

We studied the structural evolution of mesoscopic silica thin films grown at the air-water interface under dilute, acidic (pH 2-3) conditions. Our transmission electron microscopy observations reveal that the film is initially amorphous. Over time, meso- to micrometer ordered regions, enriched in the nanoscale film, resulting in a film with hexagonally packed channels mainly parallel to the air-water interface. Scanning electron microscopy revealed structural evolution at larger length scales - including ribbons, protrusions, domain boundaries, microcavities and pits. Our work confirms previous reports of a disordered structure early in the process and shows that the film develops mesoscopic order through a solid-state crystallization of the amorphous structure. Our observations suggest that the interface plays a determining role in the microstructural evolution of the films. Based on these observations and previous work, we extend the current understanding of the structural evolution of the film by providing a detailed mechanism for the transition to order.

**FS.71**

CARBOXYLATE-ALUMOXANES: APPLICATIONS AS PRECURSORS FOR AN ALUMINA ULTRAFILTRATION MEMBRANE AND HETEROGENEOUS CATALYSTS.

Christopher D. Jones, Rice University, Department of Chemistry, Houston, TX. Andrew R. Barron, Rice University, Department of Chemistry and Department of Mechanical Engineering and Materials Science, Houston, TX.

Carboxylate-alumoxanes are organic substituted alumina nano-particle, which can be synthesized from boehmite in a transparent solution which are inexpensive and environmentally benign precursors for the fabrication of nano, meso, and macro scale aluminum based ceramics. The purpose of this paper is to describe the applications of carboxylate-alumoxanes currently being researched in our laboratories.

The first application which will be discussed is the use of carboxylate-alumoxanes as a precursor to alumina ultrafiltration membranes. It has been discovered that the calcined material exhibit very narrow size distributions with near pore sizes at the low end of the mesoporous scale. Particle size and porosity can be controlled by chemical methodology. Pores in this range are normally very difficult to obtain by traditional soild techniques. Another application that will be discussed is the use of carboxylate-alumoxanes as a precursor for heterogeneous catalysts. The ability to perform further chemistry on the organic part of the carboxylate-alumoxanes allow for attachment of catalysts. During calcination, the organic ligands are burned out, leaving behind the catalyst in a well dispersed manner. Characterization of the active catalyst site will be discussed.

**FS.72**

SURFACE STRUCTURE OF NANOPHASE TITANIA. Victor Lucas, John Bartlett, Darren Attard, Jim Woolfrey, Materials Division, Australian Nuclear Science and Technology Organisation, Menai, AUSTRALIA.

Anatase and rutile are the two most common polymorphs of titanias and are widely used in applications such as catalyst, photocatalysis, and dyesensitized photovoltaic cells. Nanocrystalline titania often exhibits unique electronic and/or surface chemistry, although the relationship between these properties and the structure of the surface is not well understood. To investigate the relationship between nanocrystal dimenscions and surface structure, a series of anatase and rutile nanopowders were prepared by sol-gel processing, with crystallite sizes of 20 to 130. The corresponding fractions of surface Ti (IV) sites were ca. 60 to 10 percent for the anatase series, and 50 to 8 percent for the rutile series. The nanopowders were characterized by a wide range of techniques, including XAS, XRD, TEM, FTIR/Raman spectroscopy and TGA. The XANES spectra of the anatase nanoparticles, were strongly dependent on the crystallite dimensions, and the observed changes can be interpreted in terms of the distortion of the initial octahedral Ti (IV) environment. No such size dependence was observed for the XANES spectra of rutile nanoparticles. EXAFS revealed that the average Ti (IV) environment (surface and bulk Ti (IV) sites) in the smallest anatase nanoparticles was distorted, with contracted Ti-O bonds and reduced Ti-O coordination numbers. The results suggest that the surface Ti (IV) sites in anatase are coordinately unsaturated (presumably with five-fold Ti-O coordination), whereas the rutile surface sites exhibit six-fold Ti-O coordination.

**FS.73**

NANOPOROUS ALUMINA FILMS PREPARED FROM COLLOIDAL SOLUTION. Vladimir Petrovsky, Harlan U. Anderson, Tixiina Petrosky, University Missouri-Kansas, TAMARC, MO.

Nanoporous alumina films are of interest for such applications as high surface area catalyst support, interface layers for gas separation membranes on porous substrates, low dielectric constant plasma coatings, etc. Alumina films were prepared by spin coating and dip coating from water colloidal solutions of small (50nm) hydrophilic particles. Special components were used to stabilize solution, to improve wetting and adhesion. Platinum, silicon and alumina were used as the substrates. The resulting film thickness ranged from 1µm to 10µm. No cracking or delamination from the substrate occurred during the deposition process and the temperature range under investigation (up to 1000°C for Si substrate and up to 1500°C for alumina and Pt substrates). The phase transitions from boehmite to a-alumina and then to α-alumina were investigated by XRD analysis. The quality of the depositions were evaluated by SEM and AFM. Roughness of the surface before deposition and after deposition of the films from different precursors was measured by the mechanical profilograph to characterize plasma coating effect. Ellipsometric and spectroscopic reflection measurements were used to characterize optical properties of coatings as well as to calculate the thickness and refractive index of the films. The resulting 90% dense films were optically smooth with pore size of about 50 nm, refractive index of 1.38 and dielectric constant less than 3. Such films were able to plane substrates with roughness up to 10µm.

**SESSION F9: NANOPORES AND NANOSPHERES**

Chair: Jeffrey A. Edmundson and Greg B. Hoffland
Thursday Morning, December 2, 1999
Salon F (M)

8:30 AM

**F9.1**

CHARACTERIZATION OF BISMUTH NANOWIRE ARRAYS BY TRANSMISSION ELECTRON MICROSCOPY. Melissa Snyder, U.C. Berkeley, Dept of Chemistry, Berkeley, CA. Yu-Ming Lin, MIT.
Arrays of bismuth nanowires have attracted recent attention due to their interesting transport properties and potential for application as thermoelectric materials. In this study, transmission electron microscopy and electron diffraction have been employed to examine the nanostructure of these arrays. Samples were prepared by pressure injection of bismuth into nanowires, producing arrays with average wire diameters of 50-110 nm. The orientation and structure of the bismuth wires have been determined. The composition and morphology at the wire-matrix interface have also been examined.

8:45 AM F0.2
STUDIES OF THE DIELECTRIC CONSTANT OF THIN FILM BISMUTH NANOWIRE SAMPLES USING OPTICAL REFLECTOMETRY AND ELECTRON ENERGY LOSS SPECTRA. Marcie R. Black1, P.C. Ecklund2, Frank Bagro3, Bruce Dunn4, M.S. Dresselhaus5.1, MIT, Department of Electrical Engineering and Computer Science, Cambridge, MA; 2UCSC, Department of Materials Science and Engineering, Los Angeles, CA; 3MIT, Department of Physics, Cambridge, MA; 4University of Kentucky, Department of Physics, Lexington, KY.

Recently, 10 to 120 nm diameter single crystalline Bismuth nanowires have been formed inside amorphous sapphire. In a second set of samples, 50A diameter Bismuth nanowires are embedded in silica dioxide. Since this material has a small mass compared to other materials, quantum mechanical confinement is calculated to occur at the 50A diameter dimensions. Using Fourier transform infrared reflectometry and visible ultra violet reflectometry the optical properties of these nanowires as well as the Brewster angle determination of light incident on a nanowire array, we gratefully acknowledge the support of JURI subcontract B205-G-7A144-OI, NSF grant DMR-9400344, and the US Navy contract N00014-93-K-0052.

9:00 AM F0.3
SYNTHESIS OF SINGLE CRYSTAL BISMUTH-TELLURIDE AND LEAD TELLURIDE NANOWIRES. Qingbo Wei, Harvard Univ., Dept. of Chemistry and Chemical Biology, Cambridge, MA; Charles M. Lieber, Harvard Univ., Dept. of Chemistry and Chemical Biology and Div of Engineering and Applied Sciences, Cambridge, MA.

Dimensionality can play an important role in determining the properties of materials. In the case of thermoelectric materials, it has been proposed that one-dimensional quantum wires or nanowires and two-dimensional superlattices could exhibit substantially higher efficiencies compared to the corresponding bulk, three-dimensional solids. To explore such predictions we have initiated a program directed towards the controlled growth of nanowires, and herein, we report the synthesis of single crystal Bi2Te3 and PbTe nanowires by pulsed laser deposition. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) show that Bi2Te3 wires 80 nm to 210 nm in diameter and lengths exceeding 10 microns, and PbTe wires 25 nm to 60 nm in diameter and lengths to 2 microns can be readily produced by the laser ablation method. High-resolution TEM and electron diffraction show that the Bi2Te3 nanowires are single crystals with wire axes along the <110> crystal direction. TEM and electron diffraction measurements also show that the PbTe nanowires are single crystals. The transport properties of these new nanowire materials will be discussed.

9:15 AM F0.4
STRUCTURAL AND MAGNETIC PROPERTIES OF THE ELECTROCHEMICALLY DEPOSITED ARRAYS OF NICKEL NANOWIRES. H. R. Khan and K. Perrikowski, FEM Materials Department, Schleswig-Holstein, GERMANY.

Ferromagnetic nanowires of cobalt show anisotropic magnetic properties. A series of arrays of nanowires of Nickel of diameters (18 to 78 nm) and lengths (0.5 to 5 microns) were fabricated by electrochemical deposition of Nickel into the pores of alumina obtained by anodic oxidation of Al(1-x)Mg(x) substrates using sulfurous, phosphoric and chromic acid based electrolytes. X-ray diffraction investigations show that the Ni-nanowires consist of f.c.c. structure and the crystal size varies between 30 and 60 nm. Nanowires of 18 nm diameter and 5 microns length show a strong magnetic and crystallographic anisotropy and the preferred magnetization direction is along the axis of the nanowires. The coercivity and ratio of remanent magnetization to saturation magnetization (M_r/M_s) of these nanowires are 770 Oe and 0.82 respectively. The magneto-resistance ratio (R(H)-R(0))/R(0) of the nanowires measured in the CIP geometry show a non-magnetic magnetoresistance (AMR) behaviour. The magnetic and crystallographic anisotropy of the nanowires decreases with increasing diameter. The structural and magnetic behaviour of the Ni nanowires in relation to the diameter and length as well as to the layer of 50 nm deep aluminium deposited on Nickel substrate will be discussed.

10:30 AM F0.7
VANADIUM OXIDE NANOTUBES: STRUCTURE AND PROPERTIES. F. Kramlich, H.-J. Multer, M. Niederberger, F. Bieri, M. Reinsch, R. Nesper, Laboratory of Inorganic Chemistry, ETH Zurich, SWITZERLAND.

Vanadium oxide nanotubes (VOx/NTs) were obtained as the main product in a sol-gel reaction followed by hydrothermal treatment from vanadium(V) alkoxide precursors and primary amines (C6H13OH)2 or α,ω-diamines (H2N(CH2)4NH2 with H2N(CH2)6NH2). [1,2] The amine acts as structure-directing templates. This synthesis procedure provides an easy access to large quantities of novel tubular form of a vanadium oxide with mixed valency (V3+/V5+).

TEM images show that the length of the tubes is up to 15 μm; their outer diameters range from 15 to 150 nm and their inner diameters from 5 to 50 nm. The tube walls consist of 2-3 crystalline vanadium oxide layers. The structure within the VOx layers gives rise to a square lattice pattern of reflections (a=0.61 nm), which is the same in all tubes independent of the template molecule. On the other hand, the inter-layer distances (1.73-8 nm) increase with the alkyl chain length.
of the template, indicating that the amine molecules are intercalated between the VO$_2$ layers. Cross-sectional TEM investigations of VO$_2$-N:S reveal that a major fraction of the tube has a serpentine morphology. Clear concentric tubule arrangements of layers like in carbon nanotubes are rarely present (<1%). The scroll-like structure is highly flexible and permits to perform numerous experiments on the tubular morphology: the organic template can either be substituted by various metal cations or via proton exchange by dimers. The option to functionize the tube walls by exchange reactions represents a promising approach for the tailoring of tubular structures and thereby for a modification of their mechanical, electrical and chemical properties. [1] M.E. Spahir, P. Bitterli, R. Nepser, M. Miller, F. Krammers, D. Rieger. Angew. Chem. Int. Ed. Eng., 1998, 37, 1269. [2] R. Nepser, H.-J. Mahr, Chimia 1998, 52, 571.

10:45 AM F2.8
SYNTHESIS OF TUNGSTEN DISULFIDE NANOTUBES AND THEIR USE AS TIPS IN SCANNING PROBE MICROSCOPY. Aude Rothchild, Sidney Cohen, Reshef Tenne. Department of Materials and Interfaces, Weizmann Institute, Rehovot, ISRAEL.

Synthesis of various inorganic nanotubes from layered compounds has been described in the past. However, the synthesis of large amounts of a single phase of long inorganic nanotubes has not been reported yet.

We have recently devised a method for growing a pure WS$_2$ nanotube phase. The strategy of the synthesis and the growth mechanism will be discussed. Multiple wall nanotubes 3-10 nm in length were obtained. While most of the nanotubes have a cross section diameter of about 30 Å, at the periphery of the tube, the other nanotubes were observed. Amongst the applications, which are envisaged for these nanotubes, for tip applications in scanning probe microscopy (SPM) is most tempting. Using a previously reported method the nanotubes have been applied to the tips of the normal force microscope with various surfaces. In particular, due to their robustness and passivity, they seem to be ideally suited for examining rough surfaces with high aspect ratio features.

11:00 AM F2.9
SILICON CARBIDE NANOWIRES GROWN BY HOT FILAMENT CHEMICAL VAPOR DEPOSITION. Xinna Zhou, H.Y. Peng, N. Wang, S.T. Lee. City University of Hong Kong, Hong Kong, CHINA.

Silicon carbide nanowires have attracted a great deal of attention in recent years for their potential uses as a high-temperature semiconductor and a reinforcing element for nano-composite materials. SiC nanowires were usually grown on carbon nanotubes, on carefully prepared silicon wafers or on active carbon substrates. In present study, we grow SiC nanowires by a simple hot filament chemical vapor deposition method. A mixture of C and SiO powder was used as the reaction source. The deposition took place on the substrate heated up to 1257K. TEM observations together with electron diffraction analysis reveal that bulk-quantity SiC nanowires with diameter of 20 nm and several micrometers in length were obtained. The shape of the SiC whiskers with a diameter of 20 nm.

Both nanowires and whiskers possess spheres or rectangle clusters at their tips, which suggest a VLS growth process. EDX analysis of individual tips indeed showed that the tip contained W, Si and C.

11:15 AM F2.10
CHAINS OF SILICON NANOPHASES SYNTHESIZED FROM MIXTURES OF SILICON AND SILICON MONOXIDE. Ning Wang, H.Y. Peng, W.S. Shi, Z.W. Pan, S.T. Lee. City University of Hong Kong, Dept of Physics and Materials Science, Hong Kong, CHINA.

The bulk-quantity synthesis of silicon nanowires has stimulated great interest because of its potentially useful optical and electronic properties of nanomaterials. Recently, a self-organized chain of crystalline silicon nanowires was fabricated via an extension of the vapor-liquid-solid (VLS) mechanism [1]. Here, we report a new synthesis of bulk-quantity chains of Si nanoparticles of 20 nm in diameter through thermal evaporation of mixed Si and SiO powders. Notably, the present synthesis requires no metal catalyst, thus the growth mechanism is similar to the oxide-assisted nanowires synthesis recently reported by us [2] and it is very different from the VLS mechanism.

High-resolution TEM observations revealed that the silicon nanoparticles in the chains have no orientation relationship with respect to the growth direction of the chains. The amorphous nanoparticles connect between the nanoparticles have equal length around 20 nm. Electron energy loss spectrum analysis shows that the amorphous material is silicon oxide. The amorphous connections of the chains could be broken easily by a focused electron beam to obtain the possibility of fabricating individual Si quantum dots. The L-V characteristic and the photocurrents of this one-dimensional array of quantum dots will be discussed. [1] H. Kohno and S. Takeda, Appl. Phys. Lett. 73 (1998) 3144. [2] N. Wang, Y.H. Tang, Y.F. Zhang, C.S. Lee, I. Bello and S.T. Lee, Chem. Phys. Lett. 296 (1999) 237.

11:30 AM F2.11
CONTROLLED GROWTH OF ORIENTED AMORPHOUS SILICON NANOWIRES VIA A SLS MECHANISM. Q.L. Hang, J.Y. Xing, H.F. Yan, D.P. Yu, Z.G. Bai, J. Xu, H.Z. Zhang, Y. Ding, S.Q. Feng. Department of Physics, National Key Laboratory of Mesoscopic Physics, and Electron Microscopy Laboratory, Peking University, Beijing, CHINA.


11:45 AM F2.12
LARGE-SCALE SYNTHESIS OF AMORPHOUS SILICON NANO WIRES ON [111] Si SUBSTRATE. H.F. Yan, Q.L. Hang, J.Y. Xing, D.P. Yu, Z.G. Bai, S.Q. Feng, Department of Physics, National Key Laboratory of Mesoscopic Physics, and Electron Microscopy Laboratory, Peking University, Beijing, CHINA; G. Zeng, H.G Technology Inc., Beijing, CHINA.

The nanostructured materials have been a focused research field due to their peculiar structure, novel physical properties related to materials of low dimensionality, and potential applications in future nanodevices. Using [111] Si substrate coated with a thin layer of Ni, amorphous silicon nanowires ($\alpha$-SiNWs) were prepared by heating the substrate in an atmosphere of Ar and H$_2$ at 900°C. The $\alpha$-SiNWs have average diameter around 40 nm, and length up to several micrometers. The growth mechanism of the $\alpha$-SiNWs was found inconsistent with the well-known vapor-liquid-solid mechanism [8]. Instead it was revealed that the growth of the $\alpha$-SiNWs was controlled by a solid-liquid-solid (SLS) mechanism which is an analogy of the VLS mechanism. Green-blue luminescence was evident for the $\alpha$-SiNWs. The physical origin of such a photoluminescence from the $\alpha$-SiNWs is attributed to the oxidized surface of the nanowires.
SESSION F10. NANOPHASE METALS AND SIMULATION STUDIES
Chair: Polian, Thursday Afternoon, December 2, 1999
Salon F (M)

1:30 PM F10.1
SYNTHESIS OF MONDISPERSE COBALT NANOCRYSTALS
WITH CONTROL OVER THEIR SIZE, SHAPE, AND INTERNAL CRYSTAL STRUCTURE.
Dmitry P. Dinogu, M.G. Bawendi, MIT, Dept. of Chemistry, Cambridge, MA.

The preparation of uniform magnetic nanoparticles with control over both
as many parameters as possible has always been attractive from
both a scientific and technological point of view. Metallic particles
due to their strong magnetic properties are of particular interest.
Here we present a simple technique which enables such control.
Thermal decomposition of dihydrogen tetracarbonyl in solution in the presence of
various coordinating ligands and stabilizing agents leads to the formation of crystals
over their size, shape, and internal crystal structure. The size distribution is further
improved by size-selective precipitation, which yields nearly
monodisperse spherical particles. The size of the particles may be
varied in 3.13 nm range by simply changing the relative concentrations of the
reactants. The crystal structure, controlled by an appropriate
coordinating ligand, can be changed from primary for octocobalt.
These nanoparticles can be dispersed in a variety of non-polar solvents
forming stable colloidal solutions. A technique for assembling these
nanocrystals into 2D and 3D supercrystals is also presented. The
particles as well as their assemblies are characterized by X-ray and
electron diffraction combined with structural simulations,
transmission electron microscopy, and SQUID magnetometry.

1:45 PM F10.2
STRUCTURAL CHARACTERIZATION OF MONDISPERSE COBALT NANOCRYSTALS.
Hugh Doyle, Showeng Sun and C.B. Murray, IBM T.J. Watson Research Center, Yorktown Heights, NY.

High temperature, solution phase synthesis is coupled with size
selective processing techniques to produce organically passivated
nanocrystals with size distributions less than 5%. A series of small and wide angle x-ray scattering and electron microscopy studies are
combined with detailed computer simulations to correlate structural
data and magnet properties of cobalt nanoparticles. Studies are extended to the structural investigation of self-assembled nanocrystal
superlattices as model systems in which to study the electronic
coupling of neighboring particles. Procedures developed are not
limited to Cobalt Nanocrystals but provide general methods for the
dispersed nanocrystal and ordered nanocrystal structures from a
variety of nanocrystal based materials.

2:00 PM F10.3
SYNTHESIS AND CHARACTERIZATION OF RESORCINARENE-ENCAPSULATED NANOPARTICLES.
Alexander Wei, Stephen V. Pauzauskie, Kevin B. Stuehler, Robert I. Lefkowitz, Purdue Univ., Dept. of Chemistry and Chemical Engineering, West Lafayette, IN.

A novel class of surfactants based on the calix[4]resorcinarenes have
demonstrated unique abilities to encapsulate and stabilize near-neutral
gold nanoparticles in organic solution. These surfactants are several
times more efficient at capturing aerosol-generated particles than alkamethyls, and are able to maintain nanoparticles of up to 20 nm in
dispersed state over a period of several months. Encapsulation is
mediated by the chelation of multiple heterocyclics on the
resorcinarene hexagon to the Au surface, as characterized by surface enhanced Raman spectroscopy (SERS). Cross-linking the
resorcinarenes enhances the robustness of the encapsulated system,
allowing the particles to survive a wide range of chemical
environments and processing conditions. Characterization by electron
microscopy, gel permeation chromatography, and other physical
methods will be discussed.

2:15 PM F10.4
NOVEL ROUTES TO MONDISPERSE FUNCTIONALIZED METALS.
Mark Green, Paul O’Brien, Dept. of Chemistry, Imperial
College of Science, Technology and Medicine, South Kensington,
London, UK.

Metal nanoparticles have potential applications as memory devices
dependents. The preparation of monodisperse quantum dots of
denisc, gold and chromium passivated by several Lewis base ligands is
discussed. The dimensions of the passing ligand appears to effect
the final structural properties of certain nanoparticles. Specific metal
and Lewis base capping agents have a propensity to induce nanowire
formation, whilst other metal/capping agents systems form
nanoparticles of various morphology and sizes. NMR and IR
spectroscopies are used to investigate the gasifying ligand, whilst

HITFEM and XRD are used to investigate the structural properties of the
metal crystals. The organization of monodispersed nanoparticles
into superlattices (colloid crystals) is discussed. The effect of other
organic species in the formation of colloidal crystals is
discussed and the effect on the directional crystallization is described.

2:30 PM F10.5
DENDRIMERIC-ENCAPSULATED METAL NANOCLUSTERS:
SYNTHESIS, CHARACTERIZATION, AND APPLICATIONS TO CATALYSIS.
Richard M. Crooks, Mingxia Zhao, Victor Chechik, Li Sun.
Texas A&M University, Department of Chemistry, College Station, TX.

In this talk we describe a general template-based method for preparing
stable metal nanoparticles and demonstrate their use as homogeneous
catalysts in aqueous and nonaqueous solvents. Our approach involves
the use of polyamidoamine (PAMAM) Starburst dendrimers as both
template and stabilizer. These dendrimers are nearly monodisperse,
hydrophilic-hydrophobic polymers, which can be further
functionalized, sterically crowded on the exterior, and somewhat
hollow on the interior. We have found that transition-metal ions, including
Cu(II), Pd(II), Ru(III), and Ni(II), partition into PAMAM
dendrimers where they are strongly complexed by interior functional
groups. The number of complexed metal ions per dendrimer can be
nearly monodisperse. Thus, by preloading a dendrimer nanotemplate
with suitable metal ions and then chemically reducing this composite
in situ, dendrimer-encapsulated, zerovalent metal cluster results,
which contains the same number of atoms as were loaded into the
dendrimer as ions initially. These structures have high catalytic
activity for hydrogenation of nitrocompounds indicating that the
metal particle surfaces are active. Moreover, the dendrimer exterior
also can act as a nanofilter that admits exclusively linear isomers to the
catalytic metal particle, resulting in selective catalysis. In addition to
gas phase solvents, the dendrimer-metal complex is also soluble in
aqueous solutions and can also be resolved solubile in nonaqueous solvents. This is
accomplished by addition of a fatty acid to the nonaqueous phase. The fatty acids
surround the dendrimers in a 1:1 stoichiometry to yield structures akin to monodisperse inverse micelles. In this configuration, the
nanostructures show interesting catalytic activity for a number of
technologically important reactions, including the Wacker process. By
lowering the pH of the aqueous phase, the dendrimer-encapsulated metal nanoparticles can be reextracted into the aqueous phase.

2:45 PM F10.6
SUPERMICRO CLUSTER BEAM SYNTHESIS OF NANOPHASE MATERIALS.
P. Milani, P. Finessi, E. Barilloni, INFN-Dipartimento di Fisica, Universita di Milano, Milano, ITALY; S. Iannotta,
CEPFA-CNR, Povo di Trento (TN), ITALY.

We will present the principles and the characteristics of supermicronject beam deposition as a viable technique for the synthesis of
nanostructured films. The use of supermicronject expansions can improve the deposition rate and favor a better control on cluster mass
distribution, thus making this technique competitive with and
to other synthetic methods. The cluster source is based on the condensation of the material removed from a target by a pulsed
sputtering process. After the condensation the cluster are expanded into the vacuum to produce a supermicronjet expansion. With this source,
intense and stable cluster beams can be produced allowing film
deposition rates up to several tens of nm/min over large surfaces.
Cluster mass distributions and kinetic energies of the clusters can be
controlled prior to deposition by time-of-flight mass spectrometry.
By supermicronjet effects of typical supermicronject beams it is possible
select different mass distributions of neutral clusters in the beam,
allowing the deposition of thin films with controlled nanostructure.
Supermicronject cluster beam deposition (SCBD) has been applied to
produce nanostructured thin films of carbon and NiTi, structural
characterization confirms that the films retain the memory of the
precursor clusters thus presenting different properties. In view of
nanostructured film applications in microelectronics and for the
realization of sensors, the capability of SCBD of depositing patterns
and freestanding microstructures with high lateral resolution will be
demonstrated.

3:15 PM F10.7
NEW PHENOMENA IN MODERN GAS-SOLID NANO.
TECHNOLOGY.
Lazlo B. Kiss, Chang-Huan Guo, Robert Vajtii, Uppsala Univ., The Angstrom Lab, Uppsala, SWEDEN; F.
Einar Knus, Process- and Aerosol Measurement Technology, Dept. of Elektr Eng, Gerhard-Mercator-Universitat, Duisburg, GERMANY; P.M.
Ajayan, Rensselaer Polytech Inst, Dept. of Phys Sci & Eng, Troy, NY.

When we try to understand key processes in modern nanotechnology,
we often find that the satisfactory explanation of experimental
findings requires a new way of thinking compared to classical
approaches. In this talk we discuss some examples. 1) How do the size distributions of gas condensed nanoparticles

TIGHT-BINDING MOLECULAR DYNAMICS (TBMD) simulations are performed to investigate microscopic mechanisms of sintering of TiO_2 nanocrystals in both rutile and anatase phases. The simulations are based on an interatomic potential that was developed recently [Ogata et al., The Journal of Applied Physics, Sept. 15 issue (1999), in press].

We have investigated structural correlations and mechanical behavior of nanophase silica glasses using large-scale parallel molecular dynamics simulations. During the sintering process, the pore sizes and distribution change without any discernible change in the pore morphology. The height and position of first sharp diffraction peak in static structure factor shows significant differences in nanophase silica glasses relative to the bulk system. The simulations show a power-law dependence of the elastic moduli of nanophase silica glass on the density relative to the bulk silica density. Results on fracture toughness, crack-tip speed and stress distributions will be presented.

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