



Strasbourg (France)

E-MRS Spring Meeting 2003
June 10 - 13, 2003

SYMPOSIUM F

Nanostructures from Clusters

Symposium Organizers:

A. Perez, Université Claude Bernard Lyon, France

O. Puglisi, Università di Catania, Italy

Symposium Support:

Conorzio Catania Ricerche

CNR Progetto Finalizzato "Materiali Speciali per Tecnologie Avanzate II"

Papers will be published in Applied Surface Science

E-MRS 2003 SPRING MEETING

SYMPOSIUM F

Tuesday, June 10, 2003
Mardi 10 juin 2003

Morning
Matin

09:15 Opening session

Session I: Cluster preparation and manipulation
Session chair: A. PEREZ, University Lyon, France

F-I.1 09:20 -Invited- SUPERSONIC CLUSTER BEAM DEPOSITION: A NEW PARADIGM FOR THE ASSEMBLING OF NANOSTRUCTURED MATERIALS

P. Milani, INFN-Dipartimento di Fisica, Università di Milano, Italy

Deposition of clusters from the gas phase is becoming an enabling technology for the production of nanostructured materials. Among different experimental approaches, supersonic clusters beam deposition has been shown as a viable route for the production of nanostructured systems ranging from organized nanoislands to nanostructured thin films. To this goal the development of a highly intense cluster source is a necessary requisite together with the capability of size selecting the aggregates prior to deposition, while maintaining high particle fluxes.

By using a pulsed microplasma cluster source and by exploiting aerodynamical effects typical of supersonic beams it is possible to obtain very high deposition rates with a control on neutral cluster mass distribution, allowing the deposition of thin films with controlled nanostructure. Due to high deposition rates, high lateral resolution, low temperature processing, supersonic cluster beams can also be used for the micro and nanopatterning of cluster-assembled films when little or no post-growth manipulation or assembly is required. Supersonic cluster beams open new perspectives for the integration of gas-phase nanoparticles with planar technologies in view of mass production of micro and nanosystems with novel physico-chemical properties. Examples based on nanostructured carbon, carbon-metal nanocomposites and nanostructured titania will be discussed.

F-I.2 10:00 FABRICATION OF GOLD NANOPARTICLES BY FEMTOSECOND LASER ABLATION IN AQUEOUS SOLUTIONS

A.V. Kabashin, **M. Meunier**, J.-P. Sylvestre and E. Sacher, Laser Processing Laboratory, Department of Engineering Physics, École Polytechnique de Montréal, Case Postale 6079, succ. Centre-ville, Montréal (Québec), H3C 3A7, Canada, J.H.T. Luong, Biotechnology Research Institute, National Research Council Canada, Montreal, Quebec, H4P 2R2, Canada

Colloidal gold and silicon nanoparticles were produced by femtosecond laser (110 fs, 1 mJ/pulse, at a repetition rate of 1 kHz) ablation of a gold target plate in various aqueous solutions. Transmission Electron Microscopy (TEM), UV-VIS absorption spectroscopy and surface analysis were used to characterize the metal nanoparticles fabricated. It was found that both the mean size of the nanoparticles and their surface composition could be controlled by changing the laser ablation parameters and chemistry of the aqueous environment. Varying these parameters, we were able to produce almost monodisperse (dispersion of less than 1-1.5 nm) particles with a mean size of 1.5-2 nm. The gold nanoparticles exhibited a UV-VIS absorption spectrum with a maximum absorption band at 520 nm, which is typical for the excitation of the plasmon resonance in gold nanoparticles. The particles are of interest as markers for biosensing applications.

F-I.3 10:20 SIZE DISTRIBUTION OF SILVER NANOCLUSTERS INDUCED BY ION ELECTRON, LASER BEAMS AND THERMAL TREATMENTS OF AN ORGANOMETALLIC PRECURSOR

L. D'Urso, V. Nicolosi, G. Compagnini, O. Puglisi, Dipartimento di Scienze Chimiche, Università degli Studi di Catania, V.le Andrea Doria 6, 95127 Catania, Italy

Recently a huge variety of physical and chemical synthetic processes have been reported to prepare nanostructured materials made of very small (diameter < 50 nm) metallic clusters. Depending on the nature of clusters this new kind of materials possess interesting properties (electronic, optical, magnetic, catalytic) that can be tailored as a function of the particles size and shape. Silver nanoparticles have been obtained by an *in situ* reduction, enhanced by beams (ion, electron and laser) and thermal treatments of a silver organometallic compound (precursor) spinned onto suitable substrates.

Here we present the results of a study on the size distribution of such nanoparticles as a function of the different synthesis methods. It was found that the methods employed strongly affect the silver nanoparticles formation. Smaller silver nanoclusters were obtained after reduction by ion beam irradiation, as observed by using different techniques (AFM, SEM, UV-Vis).

10:40

BREAK

Session I: Continued

Session chair: O. Puglisi, University Catania, Italy

- F-I.4** 11:00 -Invited- COLLOID CHEMICAL APPROACH TO NANOCRYSTALS AND NANOCRYSTAL ASSEMBLIES
Luis M. Liz Marzán, Departament of Physical Chemistry, University of Vigo, 36200 Vigo, Spain
This talk will review some aspects of the use of colloid chemistry for the synthesis of nanocrystals with various shape, size and composition, as well as for the assembly of pre-formed nanocrystals, leading to the formation of nanostructures thereof.
The main emphasis will be given to metal and semiconductor nanocrystals, with special attention to the special optical properties that can be achieved through a careful control of synthetic conditions, surface modification and controlled assembly. Some aspects of recent advancements on colloid chemistry-based synthesis of magnetic nanoparticles and nanostructures will also be covered to show some specific aspects and properties.
- F-I.5** 11:40 NOVEL SINGLE-SOURCE INORGANIC-ORGANIC HYBRID PRECURSORS FOR THE SYNTHESIS OF ZnS-SiO₂ and CdS-SiO₂ NANOSYSTEMS
D. Angelova(a), L. Armelao(b), S. Gross(b), E. Tondello(a), G. Trimmel(a), A. Venzo(b), (a)Dipartimento CIMA, Università di Padova, Padova, Italy, (b)ISTM – CNR and INSTM, Università di Padova, Padova, Italy
The embedding of semiconductor nanoclusters in a silica matrix is currently a challenging task in advanced applications. In particular, zinc and cadmium sulphide-doped silica films have been thoroughly investigated for applications in different technological fields, especially for optics and optoelectronics. In this study, sulphide-doped silica nanosystems have been obtained by a sol-gel approach. To ensure a uniform distribution of the doping species inside the films, the use of single-source precursors for both silica and metal sulphide is particularly advantageous. To this aim, we have synthesized three thiourea-functionalised silanes: the already known (EtO)₃Si(CH₂)₃NHC(=S)NHPh (SiITu) and 1,4-[(EtO)₃Si(CH₂)₃NHC(=S)NH]2Ph (di-SiITu) and the novel compound (MeO)₃Si(CH₂)₃N[C(S)NH(C₆H₅)](CH₂)₂NH[C(S)NH(C₆H₅)] (SildiTu). The precursors were fully characterized by IR and NMR spectroscopies. Their decomposition pattern was investigated by Electron Impact Mass Spectrometry (EI-MS) and thermal analyses (TGA, DTA). The complexing behaviour was studied by IR and ¹H, ¹³C and ²⁹Si NMR measurements which confirmed the formation of stable sulphur-metal complexes with Zn and Cd acetates. The precursors were used to prepare nanostructured thin films. The doped nanosystems are currently under investigation through UV-Vis absorption spectroscopy, X-ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS) and Atomic Force Microscopy (AFM).
- F-I.6** 12:00 ORGANIZED PLANAR NANOSTRUCTURES FROM LIGAND-STABILIZED NANOCLUSTERS: A ROUTE TO MOLECULAR NANO-ELECTRONIC DEVICES
G.B. Khomutov, A.N. Sergeev-Cherenkov, E.S. Soldatov, D.B. Suyatin, Faculty of Physics, Moscow State University, 119992 Moscow, Russia and A.A. Rakhnyanskaya, Department of Chemistry, Moscow State University, 119992 Moscow, Russia and S.P. Gubin, Institute of General and Inorganic Chemistry RAS, 119899 Moscow, Russia and V.V. Kislov, I.V. Taranov, Institute of Radioengineering and Electronics RAS, 101999 Moscow, Russia
Nanoscale conductors (dots and wires of organic and inorganic nature) exhibit novel conductive properties that differ considerably from those of bulk conductors, and design and integration of such nanostructures into nanodevices is the principal step towards new electronics. Ligand-stabilized nanocluster molecules could prove to be promising components for nanoelectronic circuits: such compounds can be chemically synthesized in macroscopic quantities with uniform size, structure and composition, and, as a result, with absolutely reproducible properties of individual clusters what is of principal importance for creation of quantum nanoelectronic devices. The development of methods to fabricate ordered arrangements of chemically produced nanoclusters is very important for future applications in nanoelectronics and nanotechnology. We describe the formation and deposition of mixed Langmuir monolayers composed of inert amphiphile matrix and guest ligand-stabilized metal-core nanoclusters. Such approach allowed obtaining the ordered stable reproducible planar monolayer and multilayer nanocluster nanostructures on solid substrates. The use of Langmuir monolayers formed by amphiphilic polyelectrolytes and nanoclusters resulted in fabrication of ultimately thin monomolecular nanoscale-ordered stable polymeric nanocomposite films. Electronic transport in fabricated nanostructures was studied experimentally and theoretically. Single electron tunneling transistor based on a single nanocluster was demonstrated at room temperature using STM [1].
[1] S.P. Gubin, Yu.V. Gulayev, G.B. Khomutov, V.V. Kislov, V.V. Kolesov, E.S. Soldatov, K.S. Sulaimankulov, A.S. Trifonov, Nanotechnology, 13 (2002) 185-195.

F-I.7

12:20

SILICALITE-1/POLYMER FILMS WITH LOW-K DIELECTRIC CONSTANTS

O. Larlus(a), S. Mintova(b), V. Valtchev(a), T.H. Metzger(c) and T. Bein(b), (a)LMM, UMR-7016 CNRS, ENSCMu, UHA, 3 rue A.Werner, 68093 Mulhouse, France (b)Department of Chemistry, LMU, Butenandtstr.

11, 81377 Munich, Germany, (c)European Synchrotron Radiation Facility, ESRF, BP 220, Grenoble, France
The quest for low-k dielectric materials is especially urgent because of the continued miniaturization of the electronic devices. Potential candidates that could substitute for the currently used amorphous silica are the pure-silica crystalline microporous materials or some dense organic polymers. However, the pure-silica microporous materials deposited by spin coating do not sinter well, they form films with variable thickness and density and have a water content higher than 1 %. On the other hand, the polymer films sinter well but suffer from low mechanical stability and conductivity. Therefore, the combination of these two classes of materials may offer certain advantages in the preparation low-k dielectric films. Herein we report the preparation and characterization of composite films deposited via spin coating of a silicalite-1/polymer stable coating solution.

Uniform composite films with a thickness between 100 nm and 800 nm were prepared from stable ethanol suspensions of nanosized silicalite-1 and methylmetacrylate particles. Important information about the structure, hydrophobicity, particle size and shape of the nanosized species in the precursor solutions was obtained using in-situ DLS, HRTEM, TG/DTG, IR and ²⁹Si NMR spectroscopies. The orientation of silicalite-1 crystals in the composite films was studied by grazing incidence diffraction (GID) using synchrotron X-ray radiation. The conditions for film deposition, formation of stable coating solutions, and the characteristic features of the composite silicalite-1/polymer films will be discussed.

12:40

LUNCH

Tuesday, June 10, 2003
Mardi 10 juin 2003

Afternoon
Après-midi

Session II: Cluster surface interaction and self organization – Nucleation and growth processes of cluster based nanostructures
Session chair: R. Palmer, University Birmingham, UK

- F-II.1** 14:00 -Invited- CLUSTER AT SURFACES: ELECTRONIC STRUCTURE AND MAGNETISM
Karl-Heinz Meiwes-Broer, Armin Kleibert, Karl-Ludwig Jonas, Ralf-Peter Methling, Volkmar Senz, Joachim Bansmann and Viola v. Oeynhausen, Department of Physics, University of Rostock, 18051 Rostock, Germany
Experimental and theoretical investigations have shown that the electronic and magnetic properties of atomic clusters in the gas phase differ significantly from those of the respective bulk materials. Technical applications of clusters require deposition on supporting surfaces or embedding in a medium. The resulting system of clusters plus substrate or environment comprise new functional elements on the nanometer scale which makes them suitable for building new materials with tailored properties.
Well-defined surfaces may serve as model systems to study the interactions of clusters with their environment. Presently, only few studies of such systems are available which, nevertheless, have demonstrated deviations of the electronic and geometrical properties of deposited clusters from those of the free species which vary from slight modification to complete change. Therefore, many activities of the surface science and cluster communities are focussed on electronics and magnetism of clusters.
E.g., charge transport measurements through single clusters or cluster arrays can explore quantum effects and their possible interference with the nearby surface, which is an interesting issue for possible applications. Moreover, photoabsorption spectroscopy with synchrotron radiation enables the exploration of magnetic properties of deposited clusters. In this contribution results of STM/STS on silver clusters on Ge(001) and of X-ray magnetic circular dichroism (XMCD) on large iron clusters on Co/W(110) will be presented.
- F-II.2** 14:40 THERMAL PROPERTIES OF THIN AND THICK Ni₃Al CLUSTER ASSEMBLED LAYERS: AN ATOMIC SCALE SIMULATION STUDY
M. Hou(a), P. Moskovkin(a,b), (a)Physique des Solides Irradiés et des Nanostructures CP234, Université Libre de Bruxelles, Bd du Triomphe, 1050 Brussels, Belgium, (b) Russian Research Center Kurchatov Institute, Kurchatov sq., Moscow, Russia
Diffusion properties at inner surfaces and interfaces of Ni₃Al nanostructured materials are investigated by means of classical Molecular Dynamics with a second moment tight binding potential. Model samples prepared by Low Energy Cluster Beam Deposition (LECBD) on a metal substrate are used. The samples are at thermal equilibrium at 300K and zero external pressure. Half of the atoms are either located at pore surfaces or at cluster interfaces. In order to evaluate the influence of the substrate on the cluster film stability, two model samples are considered, stable at 300K. The first consists in a cluster layer interacting with the substrate. The second is a fragment of the first, to which periodic boundary conditions are applied in order to mimic an infinitely thick layer. The comparison of the diffusion properties of these samples was made. For both samples, atomic diffusion at surfaces and interfaces was found particularly fast and the diffusion coefficient obeys an Arrhenius law with an activation energy of 0.3 eV, similar to that found in liquid Ni₃Al. In addition, at elevated temperatures, the model thick film undergoes strong compaction, which is identified as the result of coalescence. The effect is less pronounced for the cluster film on a substrate, suggesting the latter to contribute to the nanostructure layer stability.
- F-II.3** 15:00 IN SITU GROWTH KINETICS OF GOLD NANOPARTICLES ON MgO(100) BY UHV-AFM
K. Hojrup-Hansen, S. Ferrero, **C.R. Henry**, CRMC2-CNRS, Campus de Luminy, Case 913, 13288 Marseille cedex 09, France
The epitaxial vapour growth of gold clusters(2-20 nm) on MgO(100) has been followed in situ under UHV by Atomic Force Microscopy and ex situ by TEM. After correction of the diameters measured by AFM for the convolution from the tip shape, the aspect ratio of the particles is accurately determined. The morphology of the particles is obtained by AFM (for the larger ones) and by ex situ TEM. At high temperature the gold clusters grow with the equilibrium shape (a truncated octahedron). This shape is preserved up to the coalescence stage where the particles become flatter. After coalescence the spontaneous reshaping towards the equilibrium shape is kinetically hindered. The particles retrieve their equilibrium shape by growth. Gold clusters grow in two epitaxies: (100) and (111) giving two different axial symmetries (four-fold and three-fold) of the equilibrium shape. In both cases the aspect ratio at the equilibrium is close to 0.6 and the adhesion energy has been determined.

F-II.4 15:20

ORGANIZATION OF NANOCCLUSERS ON FUNCTIONALIZED SURFACES

B. Prével(a), L. Bardotti(a), S. Fanget(a), P. Mélinon(a), A. Perez(a), J. Gierak(b), G. Faini(b) and D. Maily(b), (a)Laboratoire de Physique de la Matière Condensée et Nanostructures (LPMCN), UMR 5586 CNRS, bâtiment L. Brillouin, 6 rue Ampère, Domaine Scientifique de La Doua, 69622 Villeurbanne, France, (b)Laboratoire de Photonique et de Nanostructures, CNRS-LPN, Route de Nozay, 91460 Marcoussis, France
Organizing particles on a substrate in the nanoscale range is a challenge which focuses the interest of many groups from both fundamental and applied points of view. In this domain, we propose a new way consisting in the deposition of preformed nanometer size clusters on an ordered array of artificial defects which are expected to act as trap for the diffusing clusters. This approach has several advantages. First, since the defects are artificially created (using a Focussed Ion Beam nanoengraving technique (FIB)), the periodicity, the size and the geometry of the defect array (and consequently of the nanoparticles one) become experimentally adjustable parameters. Second, as the nanoparticles are synthesized using a laser vaporisation source in extreme nonequilibrium conditions, one can deposit on the patterned surfaces metastable structures or alloys of tunable size and composition. Nanosize gold clusters on Highly Oriented Pyrolytic Graphite (HOPG) has been chosen as model system in order to point out the potentialities of the technique to organize nanostructures on patterned surfaces.

Therefore, we report here on the functionalization of the substrate by analyzing the dependence of the nature of the defects on the experimental FIB parameters. Then, the evolution of gold-nanoparticles organization with artificial defects nature and periodicity is studied experimentally and analyzed in the framework of Kinetic Monte-Carlo simulations. As an application, preliminary results obtained by Scanning Near Field Optical Microscopy on those arrays will be presented.

F-II.5 15:40

CLUSTER CRITICAL SIZE EFFECT DURING GROWTH OF Co ON THE (111) HERRINGBONE RECONSTRUCTED SURFACE OF Au

H. Bulow, I. Chado, C. Goyhenex and J.P. Bucher, IPCMS-CNRS UMR 7504, 23 rue du Loess, BP43, 67034 Strasbourg Cedex 2, France

The morphological behavior of Co clusters deposited on the herringbone reconstruction of Au(111) is addressed. The Au(111) surface is well known for its herringbone reconstruction which results in a periodic arrangement of point dislocations, each site acting as preferential nucleation site for some chemical species such as Co, Fe and Ni. Upon growth at room temperature, metals like Fe and Ni have been found to form atomic monolayer clusters while Co is known to grow in bilayer clusters. Recently, by means of variable temperature UHV-STM, we actually observed three types of morphologies of the Co clusters on Au(111), depending on deposition temperature and/or Co coverage : (i) growth of monolayer Co clusters only, (ii) growth of bilayer Co clusters only and (iii) simultaneous growth of monolayer and bilayer Co clusters. With the help of Tight-Binding Molecular Dynamics calculations and Metropolis Monte Carlo simulations, we show that such a behavior relies on the existence of a phase diagram for the mixing of monolayers and bilayers: in this scheme the relative stability of the monolayer and bilayer height Co clusters is dictated by a cluster critical size of about twenty Co atoms. We show that considerations based on the difference between the Co and Au surface energy and interfacial energy may explain such a cluster critical size and that any stress storage is prevented since it is found that whatever the morphology or the size of Co cluster, it always relaxes to the bulk lattice parameter with a mean distance within the islands of 0.25 nm. Finally, in this framework of the last model, predictions for other admetals such as Fe, Ni or Cu will be given.

16:00

BREAK

Session II: Continued

Session chair: C. Henry, University Marseille-Luminy, France

F-II.6 16:20 -Invited-

TWO-DIMENSIONAL SELF-ASSEMBLY OF A HEXAGONAL SUPERLATTICE OF MAGNETIC ADATOMS

Fabien Silly(a), M. Pivetta(a), M. Ternes(a), F. Patthey(a), J.P. Pelz(b), W.-D. Schneider(a) (a)Institut de Physique de la Matière Condensée, Université de Lausanne, 1015 Lausanne, Switzerland, (b)Department of Physics, The Ohio State University, Columbus, OH 43210, USA

Long-range interactions between adatoms on metal surfaces with a surface state electron have been predicted [1] and were observed recently [2-3]. To date however, this mechanism has not been observed to produce a long-range ordered adatom superlattice. Here we present the observation of a hexagonal two-dimensional superlattice of magnetic adatoms on a metal substrate. Ce adatoms, deposited at 4.8 K on a Ag(111) single crystal surface, self-assemble into large ordered hexagonal domains. We show that the periodicity of the superlattice of 32 Å is caused by the interaction of surface state electrons with Ce adatoms and that the long-range stability of the superlattice is due to a subtle balance between the sample temperature, the surface diffusion barrier, and the concentration-dependent adatom interaction potential.

[1] K. H. Lau and W. Kohn, Surf. Sci. 75, 69 (1978)

[2] J. Repp et al., Phys. Rev. Lett. 85, 2981 (2000)

[3] N. Knorr et al., Phys. Rev. B. 65, 115420 (2002)

- F-II.7** 16:40 **PROCESSING AND CHARACTERIZATION OF DEPOSITED METAL NANOCUSTER FILMS**
S.A. Koch, G. Palasantzas, J.Th. M. De Hosson, Department of Applied Physics, Materials Science Centre and Netherlands Institute for Metals Research, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
 The technique of direct deposition of clusters to fabricate nano-structured thin films has been explored allowing for a high degree of control and versatility. Clusters of metal atoms are generated by a magnetron-discharge and clustered by the gas-aggregation technique.
 In particular we have employed a cluster source capable of producing beams of clusters with a narrow size distribution, the mean diameter being typically 5-10 nm. Clusters of several metals were deposited with low energy, to both submonolayer coverage (nanoislands) and to higher thickness (cluster-assembled thin films). The materials investigated were copper, niobium, iron, and cobalt. Our characterization of these nanostructures has focused on four different aspects: (1) Growth dynamics. Atomic force microscopy was used to analyze film surface morphology as a function of film thickness. The measured scaling exponents indicate a non-linear roughening mechanism. (2) Structural aspects. Crystal structure of the supported clusters was examined using high-resolution transmission electron microscopy, and the faceted external shapes were identified as particular polyhedra. (3) Thermal stability. The effects of high-temperature annealing on oxidation behavior, cluster coalescence, and internal structure were determined. The results depend strongly on the element under consideration. (4) Magnetic properties. These were analyzed only for Co cluster films by means of a superconducting quantum interference device, as well as by magnetic force microscopy.
 (1) G. Palasantzas, S. A. Koch, J. Th. M. De Hosson, Appl. Phys. Lett. 81, 1089, 2002.
 (3) T. Vystavel, G. Palasantzas, S. A. Koch, J. Th. M. De Hosson, Appl. Phys. Lett. 82, 197, 2003.
- F-II.8** 17:00 **FORMATION OF NANO-CLUSTERS ON SILICON FROM CARBON DEPOSITION**
V. Palermo and D. Jones, Institute for organic synthesis and photoreactivity, National Research Council, Bologna, Italy
 In this work we describe the reorganisation of silicon surfaces induced by adsorption of carbon-containing molecules. Clean Si(111) and Si(100) surfaces are prepared in vacuum, and exposed to different kinds of contaminants like carbon monoxide and methanol. Upon annealing at high temperature, self-organised nanoscopic clusters of silicon carbide (diameter 15-25 nm) form on the contaminated surfaces.
 Evolution of cluster density and size with time indicates that cluster nucleation is favoured by the carbon atoms present on the surface, while cluster growth is due to the supply of silicon atoms coming from the silicon crystal. The process can be applied to partially masked silicon surfaces; in this case, the clusters are not randomly distributed on the surface, but form preferentially at the mask border. STM measurements of the clusters are presented in combination with Montecarlo simulations. These results are used to study the cluster formation mechanism and propose possible applications of this process
 Jones, D. Palermo, V. Applied Physics Letters, 2002 v. 80, p. 673
 Jones, D. Palermo, V. Materials Science And Engineering B, 2002, v.88 (2-3), p.220
- F-II.9** 17:20 -Invited- **CLUSTER FOR BIOLOGY: IMMOBILISATION OF PROTEINS WITH SIZE-SELECTED CLUSTERS**
R. Palmer, University Birmingham, U.K.
 The controlled deposition of size-selected clusters [1,2] represents a novel route to the fabrication of nanostructured surfaces which incorporate lateral features of size 1-100 nm. This is precisely the size scale both of biological molecules such as proteins.
 Size-selected, ionised AuN⁺ clusters (N = 1 – 100) can be pinned to the (hydrophobic) graphite surface by deposition at controlled energy. Gold presents an attractive binding site for sulphur and thus potentially for cysteine residues in protein molecules. AFM measurements in buffer solution show that (ring-like) GroEL chaperonin molecules, which contain free cysteine residues, bind to the clusters, and appear to be immobilised with the protein ring parallel to the surface. Peroxidase molecules, in which the cysteine residues pair up to form disulphide bonds, can similarly be immobilised. In both cases protein clusters are also formed. The immobilisation of proteins by a dilute array of nanoscale surface features should make possible a new generation of scanning probe measurements and/or optical measurements on protein conformation and protein-protein interactions.
 1. S. Pratontep, P. Preece, C. Xirouchaki, R.E. Palmer, C.F. Sanz-Navarro, S.D. Kenny and R. Smith, Phys. Rev. Lett. 90 055503 (2003).
 2. S.J. Carroll, S. Pratontep, M. Streun, R.E. Palmer, S. Hobday and R. Smith, J. Chem. Phys. (Communications) 113 7723 (2000); see also Nature (News & Views) 408 531 (2000).

Wednesday, June 11, 2003
Mercredi 11 juin 2003

Afternoon
Après-midi

Session III: Functional nanomaterials from clusters (electronic, optical, magnetic... properties)

Session chair: G. Faraci, University Catania, Italy

- F-III.1** 14:00 -Invited- TIME-RESOLVED SPECTROSCOPY: A TOOL FOR ANALYZING METAL CLUSTER ELECTRONIC AND VIBRATIONAL PROPERTIES
Pierre Langot, Natalia Del Fatti, Dimitris Christofilos and **Fabrice Vallee**, CPMOH, Univ. Bordeaux I, 351 Cours de la Liberation, 33405 Talence, France
The optical response metals is directly related to its electronic and vibrational properties. In the case of clusters, it is also strongly influenced by the surface and environment. This strong connection is making the optical response of a nanostructured material a very sensitive probe of the nano-object properties and environment that can be exploited in the time or spectral domain to extract information on nanomaterials. In the time-domain, time resolved optical techniques have recently emerged as powerful tools for the investigation of the electron kinetics and the related fundamental electron interactions processes in metallic materials. Depending on the excitation and probing conditions, direct information on electron-electron and electron-phonon interactions can be obtained. In the case of noble metal clusters, an intrinsic confinement induced increase of the electronic interactions has been demonstrated [1]. After recalling the principle of these techniques we will discuss their application to the study of the electronic and vibrational properties of spherical nanoparticles and core-shell materials. In the spectral-domain, experiments have been essentially limited to the investigation of a very large number of metallic nanooject. Their individual response due to their shape, size or environment fluctuations are thus difficult to address. With the development of new far-field spectroscopic techniques [2], single nanoparticle spectroscopy is now possible. We will discuss their application and possible developments.
[1] C.Voisin, N.Del Fatti, D.Christofilos and F.Vallée, J. Phys. Chem B 105, 2264 (2001)
[2] D. Boyer, P. Tamarat, A. Maali, B. Lounis, and M. Orrit, Science, 297, 1160 (2002))
- F-III.2** 14:40 OPTICAL THIN FILM FORMATION BY OXYGEN CLUSTER ION BEAM ASSISTED DEPOSITIONS
N. Toyoda, I. Yamada, Laboratory of Advanced Science and Technology for Industry, Himeji Institute of Technology, 3-1-2 Kouto, Kamigori, Hyogo, 678-1205, Japan
High-quality Ta₂O₅/SiO₂ and Nb₂O₅/SiO₂ were deposited with oxygen gas cluster ion beam (O₂-GCIB) assisted deposition at low-temperature for optical filters. As one cluster ion has thousands of O₂ molecules, equivalently low-energy ion irradiations (a few eV/atom) are realized at several keV of total acceleration energy. Due to the dense energy deposition of cluster ions, high-temperature and high-pressure conditions are realized at the impacted area, which enhances chemical reactions and enables to deposit high quality thin films without heating the substrate. Also, GCIB shows significant surface smoothing effects, which realizes very flat surface and interfaces for multi-layered structures. In this study, O₂-GCIB was applied to form high quality optical films. With gas cluster ion assisted deposition, high refractive index and very smooth surface of Ta₂O₅ films were deposited. The optimum cluster ion energy and cluster ion current density for Ta₂O₅ films were found to be 7keV and 0.5μA/cm², respectively. Structure of the film was very uniform and no porous or columnar structures were observed. The surface or interfaces of Ta₂O₅/SiO₂ films were also very flat with O₂-GCIB irradiations even though the bottom surface was rough. There was no wavelength shift of filters after environmental tests, which indicates that dense oxide films were formed at low-temperature with O₂ cluster ion assisted deposition.
- F-III.3** 15:00 NON LINEAR OPTICAL ACTIVITY IN Ag-SiO₂ NANOCOMPOSITE THIN FILMS WITH DIFFERENT SILVER CONCENTRATION
A.A. Scalisj, G. Compagnini, L. D'Urso, O. Puglisi, Dipartimento di Scienze Chimiche dell'Università degli Studi di Catania ed Istituto Nazionale di Fisica della Materia (INFN), V.le Andrea Doria 6, 95127 Catania, Italy
Silica thin films (~ 1mm) have been obtained with embedded Ag nanoparticles with a controlled size distribution, using a chemical approach. Our method is able to give Ag concentration in the range of 0-10 % in weight. Several characterization techniques reveal that the particle average size is independent of silver concentration. In this paper we report a detailed analysis of the non linear optical properties of these nanocomposite thin films as function of the Ag cluster density. These analysis are conducted in the nanosecond regime at 532 nm. We find two different non linear regimes by changing the silver concentration. At low particle density we observe an optical limiting effect, while at higher density values the non linear absorption coefficient changes its sign promoting a reversible saturable absorption(RSA) process. A tentative explanation of the observed phenomenology will be given in terms of particle-particle interaction.

- F-III.4** 15:20 **ENHANCEMENT OF EXCITON EMISSION FROM ZnO NANOCRYSTALLINE FILMS BY PULSED LASER ANNEALING**
I. Ozerov, M. Arab, W. Marine and M. Sentis, Université de la Méditerranée, Faculté des Sciences de Luminy, UMR 6631 CNRS and FRE 2165 CNRS, Case 901, 13288 Marseille, Cedex 9, France
 The processes occurring during annealing of nanostructured zinc oxide films by ArF excimer laser are studied experimentally. The nanoclusters have been prepared by pulsed laser ablation of sintered ZnO target. These nanoparticles are condensed and crystallized in gas phase during the expansion of laser induced plasma into oxygen atmosphere and form c-axis oriented films when deposited onto quartz glass substrates. The films have been thoroughly examined by transmission electron and atomic force microscopy. Optical and lasing properties of the films were studied by photoluminescence (PL) using mercury lamp and femtosecond laser as excitation sources. The PL spectra of as-grown films consist of two bands: strong UV excitonic emission band and weak green-yellow defect-related band. The films have been annealed with laser fluences both, below and above the melting threshold in air and in hydrogen ambient. Our results shown that annealing in air modifies the intensity and spectral position of defect emission band, and annealing in hydrogen ambient suppresses this emission. However, in both cases the intensity of UV light emission increases drastically. The effects of laser fluence and annealing ambient on the optical properties of the films will be discussed. Under femtosecond laser excitation we observe the UV laser emission from ZnO nanostructured films at room temperature.
- F-III.5** 15:40 **METAL-DIELECTRIC PHOTONIC CRYSTALS FROM LATEX SPHERES COATED WITH GOLD NANOPARTICLES**
S.G. Romanov, P. Miclea, C.M. Sotomayor Torres, Institute of Materials Science & Department of Electrical and Information Engineering, University of Wuppertal, 42097 Wuppertal, Germany, A.S. Susha, Z. Liang and F. Caruso, Max Planck Institute of Colloids and Interfaces, 14424 Potsdam, Germany
 Metal-dielectric (MD) opals are in the focus of interest as photonic crystals (PhC) with wide and robust photonic bandgap (PBG). To prepare films of MD opals, the 640nm latex spheres were either (i) assembled in lattices and then opals were alternatively infiltrated with 5nm gold nanoparticles (NP) and oppositely charged layers of polyelectrolyte or (ii) coated with several layers of polyelectrolyte and Au NPs and then assembled in a lattice.
 Photonic bandgap (PBG) of MD opals were investigated by the angular-resolved reflectance spectroscopy in the visible and near-infrared ranges, the surface diffraction and scattering of the light. The surface plasmon resonance from Au NPs and the diffraction resonance on (111) planes of the opal lattice are characteristic features of Au/latex opals. Depending on the preparation method, the plasmon resonance changes from the single peak of individual Au NCs in infiltrated opals to the set of regular resonance peaks on NCs aggregates in opal from coated spheres. Modelling of latter resonances suggests shaping of aggregates in accord with the opal topology. The diffraction resonance representing the PBG evolves away from the dielectric-type behaviour with the increase of the Au content. In particular, the "blue" shift of the Bragg resonance with respect to that of purely dielectric opal was observed in the case of the low loaded opals. Further increase of the Au content up to ~50 wt.% results in broadening of the diffraction resonance and changing the sign of its angular dispersion. Emerging of novel diffraction resonance is the first observation of MD PBG in solid opal-like assemblies. Experimental data are discussed in the light of theory predictions.
- 16:00 **BREAK**
- 16:30-18:30 **POSTER SESSION I**

Cluster preparation and manipulation

- F/PL01** **CLUSTERS OF METALS WITH ORGANIC AND INORGANIC MOLECULES: LASER PRODUCTION AND CHARACTERIZATION**
 D. Scuderi, M. Speranza, Dipt. di studi di Chimica e Tecnologie delle Sostanze Biologicamente Attive, Università di Roma "La Sapienza", pl. A. Moro 5, 00185 Rome, Italy, A. Giardini, D. Catone, F. Rondino, Dipt. Di Chimica, Università di Roma "La Sapienza", pl. A. Moro 5, 00185 Rome, Italy and M. Satta, CNR-IMIP, 85050 Tito Scalco (Pz), Italy
 It is well known that free magnetic nanoclusters display novel properties including enhanced magnetic moments in ferromagnetic metals, ferrimagnetism in antiferromagnetic metals and the appearance of magnetism in non-magnetic metals. Today's challenge is to try and build some of the intrinsic novel behaviour into macroscopic materials. The talk will present the extent to which the intrinsic cluster behaviour is preserved in supported clusters and how cluster-cluster and cluster-support interactions modify this behaviour. XMCD studies of isolated mass-selected Fe clusters in the size range 180-700 atoms adsorbed on HOPG substrates and exposed in UHV show that the particles maintain a substantially enhanced magnetic moment relative to bulk Fe with about half of the enhancement coming from the orbital contribution. Coating the exposed clusters with Co increases the spin moment still further without significantly reducing the orbital component giving total moments comparable with free cluster values. Cluster-cluster interactions reduce the orbital moment to its small bulk value but a significant enhancement in the spin moment remains even in thick nanostructured films built out of clusters. Thick cluster films are shown to adopt a domainless correlated super-spin glass magnetic configuration that is very soft magnetically. This is a valuable technological attribute in high-moment films. Recent results on the switching dynamics in interacting cluster films will be presented.

- F/PL02** NANOSIZED AEI-COLLOIDAL ALUMINOPHOSPHATE ASSEMBLED IN THIN FILMS
M. Vilaseca(a), S. Mintova (b), V. Valtchev(c), T.H. Metzger(d) and T. Bein(b), (a)Department of Chemical and Environmental Engineering, University of Zaragoza, 50009 Zaragoza, Spain, (b)Department of Chemistry, LMU, Butenandtstr. 11, 81377 Munich, Germany, (c)LMM, UMR-7016 CNRS, ENSCMu, UHA, 3 rue A.Werner, 68093 Mulhouse, France, (d)European Synchrotron Radiation Facility, ESRF, BP 220, Grenoble, France
 The magnetic hysteresis and the temperature dependent magnetization of interacting assemblies of magnetic nanoparticles with random and ordered arrangement are studied by Monte-Carlo simulations. By comparison of our simulation results with magnetic measurements in Fe/Ag samples grown by Cluster Beam Deposition we conclude that strong interparticle exchange interactions are present in these samples in addition to the always-present dipolar interactions. The combined effect of these competing interactions is summarized in the following features: (a) increase of the coercive field with Fe nanoparticle concentration at temperature, (b) increase of the initial susceptibility with particle concentration at room temperature, (c) increase of the blocking temperature, (d) Strong dependence of blocking temperature on the applied field, (e) Strong deviations from Curie law. Features (d-e) are indications of a collective magnetic behavior in these samples. For ordered arrays of Co nanoparticles, as those prepared by Self-Assembly from a colloidal dispersion, we find that dipolar interactions are responsible for the following features: (a) increase of the blocking temperature with the coverage of the film, reaching a saturation value above one monolayer, (b) decrease of the blocking temperature with the cube of the interparticle distance, (c) at very low temperatures, an oscillatory dependence of the magnetization and coercivity on the layer coverage, with maxima at full monolayers. This behavior is attributed to the collective magnetization rotation induced in perfect hexagonal arrays due to interparticle dipolar interactions that have a clear ferromagnetic character.
- F/PL03** FABRICATION AND CONDUCTIVITY OF GOLD NANOWIRES BY E-BEAM LITHOGRAPHY IN NANOPARTICLE FILMS
J.L. Plaza(a), S. Jacke(a), Y. Chen(a), M. Couillard(a), J.P. Wilcoxon(b) and R.E. Palmer(a), (a)Nanoscale Physics Research Laboratory, School of Physics and Astronomy, The University of Birmingham, Edgbaston, B15 2TT Birmingham, U.K., (b)Nanostructures and Advanced Materials Department, Sandia National Laboratory, Albuquerque NM 87185, USA
 It was recently shown that nanowires with diameters down to 20-30 nm can be obtained by direct electron beam writing in thin layers of passivated gold nanoparticles. Here we present a scheme for the fabrication of gold nanowires, which allows conductance measurements of the structures. In the first step standard photolithography techniques were used to pattern gold microelectrodes on 65 nm thick SiO₂ film thermally grown on a p-Si substrate. In the second step a self-assembled layer of gold nanoclusters was deposited on the patterned wafer from solution. The passivated gold clusters (Au core diameter 4-4.5 nm) were surrounded by hexadecanethiol (C16H33S) ligands. Finally the fabrication of the nanowires was achieved by exposing the self-assembled monolayer to a 6kV-electron beam generated by a field emission Scanning Electron Microscope (SEM) equipped with an e-beam lithography control system. Scanning probe microscopy and scanning electron microscopy was used to characterise the structure of the nanowires while the first I-V measurements of these nanostructures are also reported.
- F/PL04** PALLADIUM NANOPARTICLES ON SILICON BY PHOTO-REDUCTION USING EXCIMER UV LAMPS
Q. Fang(a), J-Y. Zhang(b) and Ian W Boyd(a), (a)Dept. Electronic and Electrical Eng., University College London, Torrington Place, London WC1E 7JE, U.K., (b)Structure Research Laboratory, University of Science and Technology of China, Hefei 230026, P.R. China
 In recent years there has been enormously widespread interest in nano-materials and their size-dependent properties. The fabrication of noble metal nanoparticles have been one particularly active area of interest, whose properties strongly depend on size, shape and surface configuration. We report in this work a photochemical procedure induced by the UV lamp for the preparation of palladium (Pd) nanoparticles on silicon surface at room temperature. Palladium acetate dissolved in chloroform was used as precursor. The Pd precursor was deposited on Si-substrates using a conventional spray-on technique and was followed by UV radiation at wavelength of 172 nm. The SEM, AFM, XRD and UV-VIS spectroscopy have been used to characterize the as-prepared nanoparticles. The growth mechanism of the Pd particles and the photo-reduction induced by UV radiation are discussed. The effects of concentration of precursor, time of the UV-radiation and annealing conditions on the size and distribution of the palladium nanoparticles on Si were also investigated, and will be described.
- F/PL05** SURFACE MORPHOLOGY AND GROWTH BEHAVIOR OF MICELLE-TEMPLATED MESOPHASE THIN FILM
Chi Won Ahn(a), Theo Rasing(a), Mahn Won Kim(b), (a)NSRIM, University of Nijmegen, Nijmegen, The Netherlands, (b)Dept. of Physics, KAIST, Daejeon, Republic of Korea
 Mesophase thin films have attracted a lot of interest for applications in nano-electronic, -magnetic, and -photonics devices. We used the triblock copolymers (PEO-PPO-PEO) to synthesize mesophase thin films. These polymers form a spherical micelle and mesophase structure in solution by self-assembly. In order to template the mesophase structure, tetraethoxysilane (TEOS) was added into the solution, after which thin films were made by spin-coating. The thickness of the thin films was controlled by the PEO-PPO-PEO concentration in the solution. The microstructure of the mesophase thin films was characterized by atomic force microscope (AFM), transmission electron microscope (TEM), scanning electron microscope (SEM), X-ray reflectivity, and ellipsometry techniques. The measured thicknesses of the thin films are between 10nm and 500 nm. Lower thicknesses of the thin films have a step-structure on the surface and the step height is the same as the micelle size. The internal structure of the thin films has an ordered cubic symmetry.
- F/PL06** MOLECULAR DYNAMICS SIMULATION OF NANOCUSTER CONDENSATION AND GROWTH IN INERT GAS ATMOSPHERE
 Paul Erhart(a), P. Krasnochtchekov(b) and Karsten Albe(a), (a)Institute of Materials Science, Darmstadt University of Technology, Petersenstr. 23, 64287 Darmstadt, Germany, (b)Materials Research Laboratory, University of Illinois, 104 S Goodwin Ave, Urbana-Champaign IL 61801, USA
 Inert gas condensation has been studied by means of molecular dynamics simulations for supersaturated Ge, Si and SiC vapor condensing in Ar atmosphere. The state variables included the density of condensing vapor, and the density of clusters and their average size. Due to non-equilibrium nature of condensation, temperatures of the vapor and the clusters change with time and, in general, can be different. Three basic condensation processes nucleation, monomeric growth, and cluster aggregation were explicitly identified and the scaling of their rates was analyzed. Aggregation was observed to be the dominant mechanism of cluster growth starting from average cluster sizes of only about 5 atoms. A scaling of all the various variables of condensation is found that is different to the results kinetic theory of condensation. Finally, we compare our results for Si and Ge with those for SiC, which is simulated using a new analytic potential.

- F/PL07** GROWTH OF POLYMORPHOUS SILICON FILMS DEPOSITED BY PECVD AT 27.12 MHZ
 R. Martins(a), H. Águas(a), I. Ferreira(a), L. Ranniero(a), L. Pereira(a), E. Fortunato(a), P. Roca i Cabarrocas(b), N. Martins(a) and L. Boufendi(c), (a)Departamento de Materiais, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa and CEMOP, Campus da Caparica, 2829-516 Caparica, Portugal, (b)Laboratoire de Physique des Interfaces et des Couches Minces, Ecole Polytechnique, 91128 Palaiseau Cedex, France, (c)Gremi-ESPEO, REMI-ESPEO, 14 Rue d'Issoudun, BP 4567, 45067 Orléans Cedex 2, France
 Polymorphous silicon films consist in clusters of nanocrystals (2 to 5 nm in dimension) imbedded in an amorphous tissue. The aim of this paper is to present data concerning growth process of polymorphous silicon thin films (pm-Si:H) produced by plasma enhanced chemical vapour deposition (PECVD) using an excitation frequency of 27.12 MHz and correlate them with the properties of the films produced.
 Monitoring the plasma impedance and the self-bias allow the control of the growth process, where the condition of forming the required nanoparticles that will be incorporated in the amorphous matrix is reached when the plasma resistance is quite close to the plasma reactance. The identification of polymorphous material produced using the 13.56 MHz excitation frequency has been associated with a characteristic sharp peak that appears in the exodiffusion measurements located around 693K. The main features of the pm-Si:H films produced at 27.12 MHz are: a better plasma control and an enhanced growth rate; hydrogen content ranging from 20-22 at%; the exodiffusion sharp peak is shifted towards high temperatures (about 40 °K); the imaginary part of the dielectric function ϵ_2 determined by spectroscopic ellipsometry is larger and shifted to high energies when compared with pm-Si:H films produced at 13.56 MHz. That is, the films produced are more compact and dense, than the ones produced at 13.56 MHz, making them quite suitable for optoelectronic applications.
- F/PL08** NUMERICAL MODELING OF GAS-PHASE PLASMA CHEMISTRY AND SILICON ION CLUSTERING DURING PARTICULATE DEPOSITION
A.F. Stekolnikov, D.V. Feshchenko, T.A. Metelskiy, A.G. Galkevich, P.G. Makshov, Belarus State University of Informatics and Radioelectronics, Minsk, Belarus
 Formation of nanoparticles during plasma enhanced chemical vapor deposition of silicon is one of the attractive approaches in the fabrication of the nanocrystalline materials. The simulation of particle growth kinetics requires a time-dependent modeling of the gas-phase plasma chemistry. Currently negative ions are believed to be the precursors of silicon dust in a SiH₄ plasma. Mass spectroscopy reveals that negative ions can grow up to 60 Si atoms. We have suggested a model of gas-phase reactions of silane decomposition initiated by the electron impact with formation negative, containing up to 30 silicon atoms, and positive, containing 5 silicon atoms, hydrogenated ion clusters. In the kinetics scheme of silane decomposition 219 reactions were included.
 [...] Numerical results on negative hydrogenated silicon ion clusters point out forming of stable negative molecular cluster groups. The threshold of the appearance of main stable group of high-mass negative ions Si₁₅H₃₁‾ up to Si₃₀H₆₁‾ is in time limit 1,5·10⁻⁵ and 1,1·10⁻⁴ s. Their concentration ranges from 7,0·10⁷ cm⁻³ up to 8,0·10³ cm⁻³ for the time 5·10⁻⁴ s. They have masses bigger than those of positive ion clusters. It allows us to state confidently that the formation of a silicon dust with the particle more than 10 nm is connected with a continuum of negative clusters in a silane plasma. In conclusion we have developed theory of the negative hydrogenated silicon ion clustering in PECVD processes. Gas-phase model of silane decomposition during plasma enhanced chemical vapor deposition with formation of stable negative hydrogenated silicon ion clusters is suggested. The kinetics equations describing time dependent cluster formation are computed.
- Cluster surface interaction and self organization – Nucleation and growth processes of cluster based nanostructures
- F/PL09** COALESCENCE OF DEPOSITED SILICON CLUSTERS STUDIED BY MOLECULAR DYNAMICS
A.M. Mazzone, C.N.R.-Istituto IMM- Sezione di Bologna, Italy
 Recent studies (P.Jensen,Rev.Mod.Phys.,71,(1999)19) indicate that the understanding of cluster coalescence, under both aspects of cluster-cluster interactions and interaction and inter diffusion between clusters and surfaces, is vital for the development of techniques using clusters. In this study an effort has been made towards a systematic description of these concurring effects with reference to silicon systems. To this purpose three structures, i.e. an isolated cluster, a cluster dimer (that is a structure formed by two adjoined clusters) and a dimer deposited on a crystalline silicon substrate, have been considered. Isothermal molecular dynamics with classical forces describes the evolution of the three systems under the effect of a temperature increase. The study of the isolated cluster shows the inherent stability against melting and evaporation which arises from the cluster structure and size. Alterations to these properties due to the presence of a neighboring cluster are illustrated by the dimer while the study of the deposited dimer illustrates substrate effects. The combined comparison of the three cases allows to identify the functional relationship between the properties of the growing film and the ones of the isolated cluster and this should offer simple and useful suggestions for optimal deposition conditions.
- F/PL10** CLUSTER BEAM STEERING ONTO SILICON SURFACES: A STUDY BY MOLECULAR DYNAMICS
A.M. Mazzone, C.N.R.-Istituto IMM- Sezione di Bologna, Italy
 The purpose of this study is to investigate the effects of the impact conditions on cluster deposition in silicon and is motivated by recent results obtained for metallic systems (S.vanDijken et al. Phys.Rev.B.,61(2000)14047). Accordingly deposition of silicon clusters with a kinetic energy in the range from 0.5 to 10eV/atom directed at normal and grazing incidence onto crystalline silicon has been studied using classical molecular dynamics. The clusters are either crystalline fragments or are obtained from a quantum mechanical minimization of the total energy. The focus of the calculations is on channeling effects, due to the orientation of the beam and of the exposed surface, and on steering effects due to distant interactions between the cluster and the exposed surface. The general indication is that the presence of multiply coordinated atoms enhances the cluster stability and favors the formation of deposited microstructures. However clear trends are observed for a size N in the range 30-100. For these large clusters maximum fragmentation occurs for a normal incidence onto (100) while the spreading is reduced for a grazing incidence onto (100) or for a normal incidence onto (110). Compact clusters, obtained from the quantum mechanical procedure, show an enhanced resilience against fragmentation.
- F/PL11** CHARACTERIZATION OF GRAIN SIZE DURING GROWTH OF THIN METALLIC FILMS
R. Miranda and A. Cadilhe, Centro de Física da Universidade do Minho, 4710-057 Braga, Portugal
 We present an extensive Monte Carlo study of a generalized two-species ballistic deposition model with an effective attractive potential between like species and different wetting characteristics between complementary species. We study the size distribution of the grains formed during deposition for different relative rates of the incoming flux of the different species. In particular, we consider no surface mobility, thus mimicking the physically relevant limit of high activation energy barriers or high flux of incident particles. We characterize the size distribution in terms of their cumulants and also extract the values of the skewness and kurtosis to easy comparison with experimental results. This work might be of interest to people working in the production of thin metallic alloys.

- F/PL12** STM AND FIB NANO-STRUCTURATION OF SURFACES FOR LOCALIZATION OF InAs / InP (001) QUANTUM DOTS
J. Kapsa, Y. Robach, G. Grenet, G. Hollinger and M. Gendry, LEOM, UMR CNRS 5512, Ecole Centrale de Lyon, 36 avenue Guy de Collongue, BP 163, 69134 Ecully Cedex, France, J. Gierak, D. Mailly, LPN, route de Nozay, 91460 Marcoussis, France
 Controlling the nucleation of semi-conductor quantum dots is of main interest since the Stranski-Krastanov growth mode, which provides self-organized quantum dots, is unable to produce size-controlled nanostructures at intended positions, as needed for most applications.
 The site-controlled self-organization method is based on the enhancement of nucleation at specified positions. This can be caused by local modification of step density or/and strain. Modifying the morphology of the growth surface with a Scanning Tunnelling Microscope (STM) or with a nano-Focused Ion Beam (FIB) exposition can produce such local defects. The STM, connected in ultra-high vacuum to the growth chamber, appears to be a suitable method for the fabrication of nucleation sites for isolated quantum dots [1]. The FIB nanostructuring can lead to the formation of regular dense arrays of quantum dots. The STM tip was used to modify surfaces of AlInAs and InAs MBE-grown on InP(001). Bias from 3 to 10 V of both polarities were applied between the tip and the surface for times from 10 seconds to 5 minutes. Mounds and holes with diameter about 10 nm were formed, and should be suitable as nucleation sites. Regular arrays of submicron holes were formed on InP(001) by FIB nanostructuring, but possible problems of contamination or defects have to be resolved.
 [1] Kohmoto, Nakamura, Nishikawa and Asakawa, J. Vac. Sci. Technol. B 20(3), 762
- F/PL13** MORPHOLOGY CHARACTERIZATION OF LAYER-BY-LAYER FILMS FROM PAH/MacoDR13: THE ROLE OF FILM THICKNESS
 Nara C. de Souza(a), Valtencir Zucolotto(a), Josmary R. Silva(a), Felipe R. Santos(a), David S. dos Santos Jr.(a), José A. Giacometti(b), Oswaldo N. Oliveira Jr.(a), (a)Instituto de Física de São Carlos, Universidade de São Paulo, CP 369, 13560-970 São Carlos, SP Brazil, (a)Faculdade de Ciências e Tecnologia, Universidade Estadual Paulista, CP 467, 19060-900 Presidente Prudente, SP Brazil
 We report on the use of dynamic scale theory and fractal analyses in the study of very early growth stages of layer-by-layer (LBL) films of poly(allylamine hydrochloride) (PAH) and a side-chain substituted-azobenzene copolymer (Ma-co-DR13). The LBL films were adsorbed on glass substrates and characterized with atomic force microscopy (AFM) with the MacoDR13 at the top layer. The granular morphology exhibited by the films allowed the observation of the growth process inside and outside the grains. The growth outside the grains was found to follow the Kardar-Parisi-Zhang (KPZ) model, presenting fractal dimensions of ca. 2.6. One could expect that inside the grains the morphology would be that of an Euclidian surface with fractal dimension of ca. 2 for any growth stage. The latter, however, was observed only for thicker films containing more than 10 bilayers. For thinner films the morphology is well described by a self-affine fractal. Such dependence of the growth behavior with the film thickness is associated with a more complete coverage of adsorption sites in thicker films due to diffusion of polymer molecules.
- F/PL14** ADVANTAGES OF LPE FOR HETEROEPITAXIAL GROWTH OF Si_{1-x}Gex NANOSTRUCTURES
A.-K. Gerlitzke(a), H. Wawra(a), T. Boeck(a), K. Schmidt(a), Th. Teubner(a), S. Christiansen(b), M. Hanke(c), (a)Institut für Kristallzüchtung, Max-Born-Straße 2, 12489 Berlin, Germany, (b)Institut für Werkstoffwissenschaften, Lehrstuhl Mikrocharakterisierung, Universität Erlangen-Nürnberg, Cauerstraße 6, 91058 Erlangen, Germany, (c) nstitut für Physik, Humboldt-Universität zu Berlin, Hausvogteiplatz 5-7, 10117 Berlin, Germany
 The fabrication of coherent quantum dots by heteroepitaxial growth requires the understanding and control of the growth mechanism. Growth methods like MBE and CVD which have very high driving forces have a complex interplay of kinetics and thermodynamics. LPE has the advantage to run with very low driving forces close to thermodynamic equilibrium and is thus better capable to study growth mechanism.
 SiGe pyramids have been grown on silicon substrates by LPE using bismuth as solvent. The goal of the experiments is to create regularly distributed islands with a size less than 10 nm suitable for the production of quantum dot devices. As it has been shown before [1] it is possible to tune the size of the growing islands by the concentration of germanium. It has been found that the lattice misfit determines the island base width due to increasing germanium content. The minimal size that can be achieved is about 30 nm. For a further reduction of size the samples were etched chemically or by ion-beam processes. As a result islands with dimensions lower than 10 nm were obtained. Another way to get smaller pyramids is a partial re-melting using a slightly undersaturated growth solution. This has also the advantage to grow a silicon cap-layer in an additional step of the same growth run. In order to investigate the morphological results of different etching procedures Atomic Force Microscopy has been carried out. Several growth stages could be revealed.
 [1] A.-K. Gerlitzke et al., Proceedings of the E-MRS 2002 Spring Meeting, Strasbourg, June 18-21, 2002
- F/PL15** SELF-ORGANIZATION OF Si-NANOCLUSTERS IN SiO_x FILMS DEPOSITED ON Si AND GaAs SUBSTRATES FOR FIELD EMITTERS
A.A. Evtukh, V.G. Litovchenko, Yu.M. Litvin, Institute of Semiconductor Physics, National Academy of Science of Ukraine, 45 prospect Nauki, 03028, Kiev, Ukraine and H. Hartnagel, O.Yilmazoglu, Technische Universität Darmstadt, Institut für Hochfrequenztechnik, Merckstrasse 25, 64283 Darmstadt, Germany
 The formation of nanoclusters from SiO_x films is promising method for creation of effective ultra small field emitters arrays. We studied the deposition of the mentioned films prepared by thermal and PE CVD methods with thickness 50-100 nm at room temperature on Si and GaAs substrate. AFM investigates demonstrated good distinguish hillocks tips on surface of films, with height up to 20nm, curvature radii of the tip about 3-5 nm. The obtained system showed good field emission (as compared to flat uncoated surface). If surface was with tips (prepared by photolithography) or after chemical etching the I-V become shifted to lower value of applied voltage due to enhancement of electric field on tip emitters.
 The influence of the covering films on the field emission stability have been investigated.

F/PL16

GROWTH AND STRUCTURE OF SURFACE NANO-ORGANIZED PLATINUM-RHODIUM CLUSTERS

P. Andreazza(a), C. Andreazza(a), N. Bouet(a), A. Traverse(b), A.-L. Thomann(c) and P. Brault(c), (a)Centre de Recherches sur la Matière Divisée, UMR 6619, CNRS-Université d'Orléans, 1B rue de la Férollerie, 45071 Orléans Cedex 2, France, (b)LURE, CNRS-CEA-Université Paris XI, Bat. 209D, 91898 Orsay Cedex, France, (c)Groupe de Recherches sur l'Energétique des Milieux Ionisés, UMR 6606, Université d'Orléans, BP6744, 45067 Orléans Cedex 2, France

The present work deals with nucleation, growth and structure of metallic clusters obtained by plasma sputter deposition on amorphous substrates. The main interest of this method is that atom deposition is assisted by low energy and high flux of argon ions. The possibility for tuning the growth in term of aggregates morphology, density and size independently of the substrate temperature is very suitable to prepare materials to controlled assemblage.

On the other hand, our works have showed that both ion flux and sputtered atom kinetic energy drive the aggregates structure in a coupled way. This property is particularly interesting to control the atomic arrangement in catalytic or magnetic bimetallic supported clusters. The goal of this study is to understand and to control the growth and structure effect of assistance ions flux in plasma sputter deposition. We report a detailed morphological and structural characterisation of sample obtained in ion flux and metal atom energy relevant parameters conducted through the combined use of several characterization techniques i.e. X-ray Absorption Spectroscopy (EXAFS), Grazing Incidence X-ray Diffraction (GIXD), Grazing Incidence Small Angle X-ray Scattering (GISAXS) and Transmission Electron Microscopy (TEM). These supported clusters (Pt, Rh, Pt-Rh) have been obtained with different average compositions and different size on amorphous silicon oxide and carbon. Different proposed models of structure and organization are in a good agreement with the experimental results. In function of plasma conditions, structural features (a preferential Rh enrichment of the aggregate surfaces or a disorderly alloy) and growth regimes (nucleation and static and/or dynamic coalescence) differ.

Functional nanomaterials from clusters (electronic, optical, magnetic... properties)

F/PL17

NANOSTRUCTURE FORMED BY MULTILAYER SI/GE/SI CLUSTERS. ROOM TEMPERATURE PHOTOLUMINESCENCE

N.D. Zakharov, P. Werner, Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle(Saale), Germany, G.E. Cirlin, A.A. Tonkikh, V.A. Egorov, A.F.Ioffe Physico-Technical Institute RAS, Polytechnicheskaya 26, 194021 St.Petersburg, Russia, V.G. Talalaev, St.Petersburg State University, 198504 Petrodvoretz, St.Petersburg, Russia

In the present work we would like to report on the fabrication of defect-free multilayer Si/Ge/Si structures exhibiting strong Photoluminescence (PL) at 1.55 μm at room temperature. The structure was grown by molecular beam epitaxy (MBE) and consist of 20 Ge layers (0.7 nm Ge in each layer) separated by 5 nm Si spacers. The first 2nm of each Si spacer were intentionally doped with Sb ($n \approx 8.776 \cdot 10^{17} \text{ cm}^{-3}$). Structure was examined by transmission electron microscopy. The lateral size of the Ge islands was about 80 nm. The average density of Ge QD is about $1 \times 10^{10} \text{ cm}^{-2}$. PL integrated intensity versus excitation density shows unambiguously super-linear behaviour $I = P^m$, with factor m equal 1.6 within a wide excitation range of 3 to 6000 W/cm^2 . Influence of different growth parameters (thickness of capping layer, thickness of Ge and Si layers, Growth temperature and annealing) on specimen's structure and PL properties will be considered.

F/PL18

SYNTHESIS AND CHARACTERIZATION OF SE NANO-STRUCTURES INSIDE POROUS ZEOLITE CRYSTALS

Irene L. Li, Z.K. Tang, Department of Physics and Institute of Nano Science and Technology, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, P. Launois, LPS (UMR CNRS 8502), bat 510, universite Paris Sud, 91405 Orsay, France

Detailed synthesis process of semiconducting selenium species incorporated in the channels of AlPO₄₋₅ zeolite single crystals was reported. Different attempts have been made to determine the nano-structures of the adsorbent. Thermal adsorption / desorption process of selenium species is studied by simultaneous thermogravimetry (TG) and differential scanning calorimetry (DSC). There exist two peaks both in the TG and DSC curves, indicating that two different structures of Se species co-exist in the zeolite channels. In the X-ray diffuse scattering pattern, several clear parallel diffuse scattering layers normal to c-axis in the reciprocal space are compatible with the existence of finite chain-like structures, while some weak scattering clouds correspond to some disordered or localized structures. Polarized Raman peaks reveal the resonant features of the well-aligned one dimensional selenium chains, as well as the random distribution of the 8-member selenium rings. Polarized optical absorption spectra confirm that the helical chains are highly aligned along the channel direction, while the Se₈ rings are randomly oriented in the channels. The helical chains have a lowest optical absorption band at 2.6 eV that is strongly polarization dependent, while the 8-member rings have a lowest absorption band at 3.0 eV that varies slowly with the light polarization, which consist well with the consequences of polarized Raman and X-ray diffuse scattering analysis.

F/PL19

OBSERVATION OF LOCALIZATION COMPLEXES AND PHONONS REPLICAS IN HEAVILY DOPED GaAs_{1-x}N_x

E. Bousbih(a), S. Ben Bouzid, R. Chtourou, J.C. Harmand(b), (a)Unité de recherche de Physique des Semiconducteurs, Institut Préparatoireaux Etudes Scientifiques et Techniques, BP 51, 2070 La Marsa, Tunisia, (b)Laboratoire de Photonique et de Nanostructures, CNRS Route de Nozay 91 460 Marcoussis, France

The electronic properties of GaAs are profoundly affected by the incorporation of low concentrations of N. A reduction of the bandgap exceeding 0.2 eV per atomic percent of N content has been observed in GaAs_{1-x}N_x for $x < 0.02$. Despite years of extensive experimental and theoretical studies, there is no general consensus on the microscopic mechanism responsible for the observed band-gap reduction in GaAs_{1-x}N_x. In the ultra-dilute regime ($x < 0.01\%$) nitrogen produces complexes levels above the conduction band minimum.

Alternatively, the alloy limit may have not been reached experimentally and the mechanism responsible for the bandgap reduction is the formation of N-clusters, which have discrete states inside the GaAs bandgap. In this work, we study the behaviours of nitrogen complexes in dilute GaAs_{1-x}N_x alloys ($x \sim 10^{18} \text{ cm}^{-3}$) grown by molecular beam epitaxy on (001) GaAs substrate and on GaAs misoriented 2°, 4° and 6° from the (001). At the first, we have found that photoluminescence measurements for as-grown GaAs_{1-x}N_x layers with (001) GaAs substrate reveals the presence of complex center with the apparition of phonon replicas at 33 or 36 meV below the complex peak. After thermal annealing for 10 min at 750 °C all the replicas disappear and the complex peak becomes dominant. Secondly, we investigate the dependence of growth temperatures on N-related emissions for two series of samples with different growth temperatures 420 °C and 470 °C and different substrate disorientations.

- F/PL.20** GROWTH AND OPTICAL PROPERTIES OF InAs/GaAs QUANTUM DOT STRUCTURES
Vladimir I. Trofimov, Institute of Radioengineering & Electronics of RAS, 11 Mokhovaya Street, 101999 Moscow, Russia, Hee Seok Park, Nano. fab., Korea Signal, Yuchang B/D 601, Yoido-dong, Youngdungpo-Gu, Seoul, Korea
 The growth and optical properties of InAs/GaAs (001) quantum dot (QD) structures depending on the deposition parameters are investigated. The epitaxial layers were grown in a Riber 32P MBE system and studied by atomic force and cross-sectional transmission electron microscopy, and photoluminescence (PL). For a single QD with 2.7ML of InAs deposited at a rate of 0.025 ML/s the dots have a dome shape and with increasing substrate temperature T_s from 4600C to 5000C their surface density decreases from $2 \times 10^{10} \text{cm}^{-2}$ to $1.4 \times 10^{10} \text{cm}^{-2}$ and the mean lateral size increases from 40nm to 70nm, the dots height doesn't exceed 5nm. At low beam equivalent pressure of As (below 3×10^{-6} torr) and higher T_s the segregation of In occurs. The multiple stacked QD structures (2.7 or 4ML of InAs with 4-ML GaAs spacer) with the more uniform morphology in the upper layers providing the intense and narrow PL spectrum are formed at $T_s = 4900\text{C}$ and the flux ratio $\text{As/Ga} = 12$. The multilayer QD heterostructures N-AlGaAs/GaAs/InAs/GaAs/InAs/GaAs/GaAs containing up to ten double layers InAs (2.7ML)/GaAs (4nm) with delta Si-doped AlGaAs barrier and a GaAs cap layer were first grown and the PL temperature behavior is studied. At low temperatures (below 90 K) one PL peak at 1.26 eV is observed, with increasing temperature it is shifted to a lower energy and the second peak on the lower energy side appears, and its intensity increases with temperature and the excitement power.
- F/PL.21** ELECTRICAL AND EMISSION PROPERTIES OF NANO-COMPOSITE SiO_x FILMS
A.A. Evtukh, I.Z. Indutnyy, I.P. Lisovskyy, Yu.M. Litvin, V.G. Litovchenko, P. Lytvyn, D. Lazunov, Yu.V. Rassamakin, P. Shepeliyavyi, A.Yu. Kizyak, Institute of Semiconductor Physics, National Academy of Science of Ukraine, 45 prospect Nauki, 03028 Kiev, Ukraine
 The electrical and emission properties of as deposited and annealed SiO_x films have been investigated in details. The films were obtained by thermal evaporation of silicon powder in vacuum (2-3) $\cdot 10^{-5}$ Torr. At the beginning the visible light absorption, IR spectroscopy and atomic force microscopy methods were used for characterization of the films. It was shown that as deposited SiO_x ($x \approx 3$) film is a nano-composite one in which the Si cluster is coated with SiO phase. At thermal annealing of the film the additional phase decomposition is observed and it transforms into SiO₂(Si) film. At low electric fields the I-V characteristics of dark current of the initial SiO_x films correspond to Frenkel-Poole transport mechanism The Fowler-Nordheim tunneling dominates at higher electric fields. As to annealed SiO₂(Si) films the modified Fowler-Nordheim electron tunneling through trapezoidal SiO₂ barrier between silicon clusters restricts the current flow. The effective electron field emission from flat silicon wafer coated with nanocomposite SiO_x films was observed as before and after thermal annealing with following refreshment by etching in HF:H₂O solution. The current peaks are appeared on emission I-V characteristics. The model for explanation peculiarities of electric conductivity and electron field emission from nano-composite films have been proposed.
- F/PL.22** STRUCTURAL AND OPTICAL PROPERTIES OF CU:SILICA NANOCOMPOSITE FILMS PREPARED BY CO-SPUTTERING DEPOSITION
 G. Battaglin, E. Cattaruzza, F. Gonella, R. Polloni, B.F. Scremin, INFN and Dipartimento di Chimica Fisica, Università di Venezia, Dorsoduro 2137, 30123 Venezia, Italy, G. Mattei, P. Mazzoldi, C. Sada, INFN and Dipartimento di Fisica, Università di Padova, via Marzolo 8, 35131 Padova, Italy
 Metal nanoclusters embedded in fused silica exhibit peculiar optical properties that have made them attractive in several application fields. Prescribed Cu:silica composite features require the control of the cluster formation and growth, and therefore the definition of effective preparation protocols.
 In this work, copper-containing silica films were synthesized by radiofrequency co-sputtering deposition technique, and then heat-treated (in some cases sequentially) in different annealing atmospheres, i.e. either oxidizing or reducing. Characterization of the samples along the various preparation steps has been performed by Rutherford backscattering spectrometry, transmission electron microscopy and optical absorption spectroscopy. Experimental observations have shown the complexity of the copper behaviour during the composite formation: copper migration and aggregation depend critically on the annealing conditions, in particular on the atmosphere, and quite different stable structures actually result. For example, in samples heat-treated first in air and then in an H₂-Ar gas mixture, the oxidizing atmosphere drives copper towards the surface while the reducing one promotes the subsequent clusterization in a well defined region. This shows how the combined preparation methodology actually provides further degrees of freedom in the control of the final composite structure. Preliminary determination has been also made of the nonlinear optical coefficient n_2 of the nanocomposite films, related to the electronic third-order optical nonlinearity. The experiment was realized by means of the Z-scan method, using a doubled-frequency Nd:glass source at 1 Hz of repetition rate.
- F/PL.23** REVERSIBLE TUNING OF SIZE QUANTIZATION IN SEMICONDUCTOR NANOCRYSTALS BY CONTROL OF INTERPARTICLE FORCES
Shira Yochelis and Gary Hodes, Weizmann Institute of Science, Materials and Interfaces, Rehovot 76100, Israel
 Semiconductor quantum dots exhibit changes in optical absorption spectra with change in dot size due to size-dependent energy level spectra. Aggregation of very small dots can decrease these changes due to charge overlap in neighboring dots. This overlap is strongly distance dependent. We show, using CdSe quantum dots aggregated in various liquids, that in the absence of capping agents, this loss in size quantization occurs for larger dots than for previously-reported capped ones, that the optical spectra of the aggregates change with time and that control of the forces between dots, mediated by the liquid, changes the kinetics and the type of interaction between nanocrystals and as a result, their spectral properties. Simple mechanical agitation, which partially breaks up the aggregates, can cause reversible changes in the spectra under conditions where the attractive forces are balanced by repulsive hydration forces. The very high sensitivity of the spectral properties to very small differences in distance between particles also allows simple visual or spectroscopic evaluation of forces between such particles.
- F/PL.24** FIELD EMISSION FROM GE Ge NANOCCLUSERS ON SI(100) UNDER INFRARED RADIATION
Yurii M. Litvin, Petro M. Lytvyn, Institute of Semiconductor Physics, NASU, Kiev, Yurii N. Kozyrev, Maria Yu. Rubezhanska, Institute of Surface Chemistry, NASU, Kiev, A.A. Dadykin, Institute of Physics, NASU, Kiev, Ukraine
 Field emission from the samples with Ge quantum dots grown on Si(100) has been investigated experimentally. It was shown that, in addition to earlier observed effect of resonant tunneling [1], the essential current amplification (≈ 10 times) was observed at the same applied voltages. Dimensional quantization is not seen on I-V plots, when the nanoislands are more than 6 nm in height [2]. However, as this takes place, the total current increases. The mechanism influencing the anomalous I-V characteristic behaviour, in particular, elastic strain in the quantum dots and nanoisland interaction with infrared heating is discussed.
 [1] A. Dadykin, Yu. Kozyrev, A. Naumovets, JETP Letters 76 (5) (2002) P. 550.
 [2] M. Rubezhanska, Tech.Dig. IVMC and IFES, Lyon, France, July 8-12 2002.

F/PL25 RAMAN AND LUMINESCENCE STUDY OF ION BEAM IRRADIATED POROUS SILICON: A CASE FOR THE ASTROPHYSICAL EXTENDED RED EMISSION?

G.A. Baratta, G. Compagnini and G. Strazzulla, INAF-Osservatorio Astrofisico di Catania, Via S.Sofia 78, Catania 95123, Italy, Dipartimento di Scienze Chimiche, Viale A.Doria 6, Catania, Italy

We have measured the photoluminescence (PL) of porous silicon thin films subjected to ion irradiation with 30 keV He⁺ ion beam. Fluence has been changed between 1014 to 1016 ions/cm². These fluences are compatible with those suffered by dust grains in some astronomical environments. Luminescence has been excited with both visible and UV radiation and the results show a decrease of the photoluminescence intensity by increasing the ion fluence, probably due to the formation of induced nonradiative recombination centres. The increase of defects density and the partial amorphization of the samples have been studied through Raman spectroscopy and a comparison with the induced damage in single crystalline silicon has been considered. The characteristic PL wavelength (600-800 nm) and the possibility to tune the PL yield over several orders of magnitude support the hypothesis that silicon nanostructures are an attractive carrier for the so called "Extended Red Emission" (ERE) observed in many astronomical objects where cosmic ion irradiation contributes to drive the evolution of these nanostructures.

F/PL26 MICROSTRUCTURAL AND OPTICAL ABSORPTION PROPERTIES OF Ag-BaF₂ COMPOSITE FILMS PREPARED BY CO-EVAPORATION

A. Rizzo and M.A. Tagliente, ENEA, CR Brindisi, SS. 7 Appia, 72100 Brindisi, Italy

Composite films consisting of ceramic matrix and embedded metal nanoparticles are attracting attention for their potential applications as low-temperature-coefficient film based resistors, optical or electromagnetic anti-reflecting layers and solar energy transform devices. In this work, we report on the investigation about the microstructural and the linear optical properties of 10-50 wt % Ag-BaF₂ composite films prepared by co-evaporation in vacuum. Sintered-in-vacuum Ag-BaF₂ mixtures with several weight ratios were used as evaporant. X-ray diffraction studies performed both in conventional and glancing incidence geometries indicate that the Ag-BaF₂ composite films are mainly composed of a polycrystalline BaF₂ fcc matrix with embedded Ag fcc nanoparticles with average sizes of 5-10 nm. The optical absorption of the films decreases as the wavelength increases in the range of 200-800 nm. The Ag-BaF₂ films exhibit a surface plasmon resonance absorption peaks from the Ag nanoparticles in the visible region (at about 500 nm). The experimental optical absorption properties have been quantitatively evaluated in the frame of the Maxwell-Garnett theory.

Thursday, June 12, 2003
Jeudi 12 juin 2003

Morning
Matin

Session III: Functional nanomaterials from clusters (electronic, optical, magnetic... properties) Continued
Session chair: P. Mélinon, University Lyon, France

- F-III.6** 8:50 -Invited- BUILDING HIGH-PERFORMANCE MAGNETIC MATERIALS OUT OF GAS-PHASE NANOCLUSTERS
C. Binns, S.H. Baker, M.G. Maher, S. Louch and S.C. Thornton, University of Leicester, U.K.
It is well known that free magnetic nanoclusters display novel properties including enhanced magnetic moments in ferromagnetic metals, ferrimagnetism in antiferromagnetic metals and the appearance of magnetism in non-magnetic metals. Today's challenge is to try and build some of the intrinsic novel behaviour into macroscopic materials. The talk will present the extent to which the intrinsic cluster behaviour is preserved in supported clusters and how cluster-cluster and cluster-support interactions modify this behaviour. XMCD studies of isolated mass-selected Fe clusters in the size range 180-700 atoms adsorbed on HOPG substrates and exposed in UHV show that the particles maintain a substantially enhanced magnetic moment relative to bulk Fe with about half of the enhancement coming from the orbital contribution. Coating the exposed clusters with Co increases the spin moment still further without significantly reducing the orbital component giving total moments comparable with free cluster values. Cluster-cluster interactions reduce the orbital moment to its small bulk value but a significant enhancement in the spin moment remains even in thick nanostructured films built out of clusters. Thick cluster films are shown to adopt a domainless correlated super-spin glass magnetic configuration that is very soft magnetically. This is a valuable technological attribute in high-moment films. Recent results on the switching dynamics in interacting cluster films will be presented.
- F-III.7** 9:30 NUMERICAL STUDY OF THE COLLECTIVE MAGNETIC BEHAVIOR OF NANOPARTICLE-ASSEMBLED FILMS
D. Kechrakos and K.N. Trohidou, NCSR "Demokritos", Athens, Greece
The magnetic hysteresis and the temperature dependent magnetization of interacting assemblies of magnetic nanoparticles with random and ordered arrangement are studied by Monte-Carlo simulations. By comparison of our simulation results with magnetic measurements in Fe/Ag samples grown by Cluster Beam Deposition we conclude that strong interparticle exchange interactions are present in these samples in addition to the always-present dipolar interactions. The combined effect of these competing interactions is summarized in the following features: (a) increase of the coercive field with Fe nanoparticle concentration at temperature, (b) increase of the initial susceptibility with particle concentration at room temperature, (c) increase of the blocking temperature, (d) Strong dependence of blocking temperature on the applied field, (e) Strong deviations from Curie law. Features (d-e) are indications of a collective magnetic behavior in these samples. For ordered arrays of Co nanoparticles, as those prepared by Self-Assembly from a colloidal dispersion, we find that dipolar interactions are responsible for the following features: (a) increase of the blocking temperature with the coverage of the film, reaching a saturation value above one monolayer, (b) decrease of the blocking temperature with the cube of the interparticle distance, (c) at very low temperatures, an oscillatory dependence of the magnetization and coercivity on the layer coverage, with maxima at full monolayers. This behavior is attributed to the collective magnetization rotation induced in perfect hexagonal arrays due to interparticle dipolar interactions that have a clear ferromagnetic character.
- F-III.8** 9:50 NANOSTRUCTURED THIN FILM FROM MIXED MAGNETIC CLUSTERS
L. Favre, S. Stanesco, V. Dupuis, E. Bernstein, J. Tuillon-Combes, A. Pérez, Laboratoire de Physique de la Matière Condensée et Nanostructures, Université Claude Bernard Lyon I, Bat. Léon Brillouin, 6 rue Ampère, 69622 Villeurbanne Cedex, France
Magnetic nanostructured films have been prepared from clusters prepared in the gas phase using the Low Energy Cluster Beam Deposition (LECBD) technique¹. Such films consist of metallic clusters obtained from a combined laser vaporization-gas aggregation source, embedded in a matrix co-deposited from an electron gun evaporator. In order to minimize the effects of the direct contact between the magnetic clusters and the surrounding matrix, we produced mixed clusters Co-M (M = Ag or Pt). The clusters stoichiometry is the mixed CoM-targets one and a core-shell morphology has been observed. In this paper, we report mainly on "nanoscopic" measurements performed on a single particle to investigate its intrinsic properties. For that purpose, thin superconducting films (Nb) containing a very low concentration of clusters (< 1 %, isolated clusters) have been e-beam lithographed to prepare ultrahigh sensitivity micro-SQUID magnetometers² to determine the origin of the magnetic anisotropy at the nanoscale. Scanning Tunneling Microscopy measurements at very low temperature³ have been carried out in view to describe the local density of state of a superconductor faced a magnetic grain. Tunneling electronic transport measurements via single magnetic particle are in progress on CoM-clusters embedded in an insulating oxide matrix (MgO).
¹ A. Perez et al. Materials Transactions, Special Issue on Nano-Metals, 1, 42, 1460 (2001).
² M. Jamet, W. Wernsdorfer et al. Phys. Rev. Lett., 86, 4676 (2001).
³ N. Moussy, H. Courtois et al. Phys. Rev. Lett., 72, 128 (2001).

F-III.9 10:10 **MAGNETIC PROPERTIES OF DENSE Co NANOPARTICLES ENCAPSULATED INTO CARBON NANOTUBES AND OTHER NANOSTRUCTURES**
C.S. Cojocaru, C. Meny, A. Derory and F. Le Normand, IPCMS, UMR 7504 CNRS, PO Box 43, Bat 69, 23, rue du Loess, 67034 Strasbourg Cedex, France
The next generation of materials for magnetic recording media will require i) the design of regular arrays of ferromagnetic nanoparticles with well controlled morphology and behaviour and ii) to physically separate these particles, either by vacuum or by a nonmagnetic material to fully discriminate the bits of information. Other requirements are the chemical stability, the obtention of a definite direction for magnetization, the mechanical stiffness... The growth of carbon nanotubes by a catalytic CVD process requires the presence of nanoscaled transition metals particles (Fe, Co, Ni), which are ferromagnetic and which act as catalysts for the carbon adsorption, diffusion and finally extrusion into nanotubes. Therefore these particles are encapsulated after growth on the top of the nanotubes. Moreover in appropriate deposition conditions they took a very anisotropic shape. Various other carbon nanostructures can be grown (nanocones, carbon nanofibers, ...), both depending on the experimental CVD and the metallic dispersion parameters. The magnetic properties of these arrays of Co nanoparticles encapsulated into carbon were investigated by SQUID and MFM. Different magnetic behaviours were evidenced
- Superparamagnetic behaviour for small particles (5 à 8 nm) encapsulated into non oriented nanotubes
- Strong magnetic anisotropy perpendicular to the plan of the substrate of metallic nanowires (diameter~25 nm and aspect ratio from 1/4 to 1/10), induced by the cork-like shape of the nanoparticles. In this case the coercive field (750 Oe), the magnetic anisotropy combined with high density (1010particles/cm²) and the weak dipolar interactions evidenced by MFM are very attractive for dense storage media.

10:30

BREAK

Session III: Continued

Session chair: F. Gonella, University Padova, Italy

F-III.10 11:00 -Invited- **STRUCTURE AND PROPERTIES OF NOBLE METAL PARTICLES FOR NANOSTRUCTURED THIN FILMS**

Giuseppe Compagnini, Chemistry Department, University of Catania and Istituto Nazionale per la Fisica della Materia, Viale A.Doria 6, Catania 95125, Italy

During the last few years one of the most important subject in chemistry and physics of nanoscale materials has been the synthesis of nanostructured thin films (0.1-1 μm) for application in optics and electronics. Particular emphasis has been given to the synthesis and properties of nanocomposite thin films with noble metal particles in insulators. Our contribution to this field has been given by obtaining and studying films consisting of a polymeric or a semiconductor oxide matrix with Au or Ag particles (5-20 nm in size) embedded at different concentrations.

To do this we exploit one of the following synthetic strategies:

- 1) chemical methods, using suitable precursors for both host and guest materials
- 2) physical methods mainly based on laser ablation As an example of the first case it is presented the possibility to obtain silver nanoparticles in a number of different polymeric thin film by using a silver metallorganic compound soluble in most organic solvents which easily decompose in metallic silver with the loss of the organic moiety. The second synthetic strategy concerns with the possibility to generate a metal colloid through direct laser ablation of suitable metallic targets immersed in the liquid itself. These colloids can be subsequently used with a "spin coating" procedure to obtain thin films in a very simple way. Properties of these and other nanocomposites will be discussed using structural and spectroscopic characterization techniques.

F-III.11 11:30

NANOSTRUCTURED FILMS FROM (C₆₀)_nSi_m CLUSTERS

B. Masenelli, F. Tournus, P. Mélinon, X. Blase, A. Perez, LPMCN Université Claude Bernard Lyon 1, 69622 Villeurbanne, France, M. Pellarin, M. Broyer, LASIM Université Claude Bernard Lyon 1, 69622 Villeurbanne, France

Cage-like covalent clusters (fullerenes) are attractive materials for the design of novel nanostructured thin films particularly when doped with atomic elements. The dopants can either strengthen the cohesion of the film (pristine fullerenes films are molecular films linked by weak van der Waals forces) or tune the electronic properties of the material.

In this prospect, we report on the synthesis, structural and physical characterization of a new material based on C₆₀ and silicon atoms. (C₆₀)_nSi_m clusters are prepared in a laser vaporisation/supersonic expansion source and deposited onto a silver coated silicon substrate (in Ultra High Vacuum) making up a nanogranular thin film (100nm thick). Auger, X ray photoemission and Raman spectroscopies as well as extended X ray absorption fine structure (EXAFS) analysis reveal an unusual environment around silicon atoms with Si atoms linked to ten or more carbon atoms (pentagon or hexagon rings) and a charge transfer from Si to C₆₀. First principle calculations confirm the stability of the structure (2 eV approximately) and the ionic-covalent nature of the bond. Therefore silicon atoms act both as binding elements between fullerenes and donor dopants. The transport properties currently under investigation should tell whether this local behaviour is kept throughout the entire film.

- F-III.12** 11:50 **A NEW CONCEPT OF VARIABLE CAPACITORS BASED ON CLUSTERS IN THE COULOMB BLOCKADE REGIME**
N. Lidgi, P. Seneor, J. Carrey, F. Nguyen Van Dau, H. Jaffrès, A. Fert, F. Petroff, A. Vaures, A. Friederich, Unité Mixte de Physique CNRS-THALES, Orsay, France
 We propose a new concept of capacitor based on the Coulomb blockade effect. The structure studied is constituted of two metallic electrodes separated by a thin (few nm) insulating film in which a 2D array of nanometric metallic clusters are embedded. The Coulomb blockade phenomenon can be observed by applying a voltage to this junction: in order to tunnel from an electrode to an isolated cluster, an electron has to overcome the Coulomb energy of the cluster. That's why, below a threshold voltage (V_t), no current is measured. If an AC voltage modulation is added to V_t , then, during each cycle the metallic island will charge and discharge itself. This charge-discharge cycle creates a small AC current between the electrode and the cluster inducing a differential capacitance peak at V_t . When an assembly of clusters is considered, the capacitance variation versus voltage will strongly depend on the cluster size distribution, as there is a different voltage V_t for each cluster size. We have developed a model that let us hope to control the voltage range and amplitude of the capacitance variation using an appropriate cluster distribution. We will present the model and also the first experimental evidence of a variable capacitor.
- F-III.13** 12:10 **EFFECT OF SPATIAL CORRELATIONS ON THE CONDUCTIVITY OF ISLAND ASSEMBLY NANOSTRUCTURES**
Vladimir I. Trofimov, Institute of Radioengineering & Electronics of RAS, 11 Mokhovaya Street, 101999 Moscow, Russia; Hee Seok Park, Nano. fab., Korea Signal, Yuchang B/D 601, Yoido-dong, Youngdungpo-Gu, Seoul, Korea
 Effect of island size distribution and spatial correlations, as observed in real island assemblies (e.g., [1]), on the electrical conductivity of these island nanostructures is studied. The treatment is based on the percolation theory according to which the conductivity in an assembly of metallic islands on insulating substrate occurs due to charge transfer along an infinite stochastic chain of coupled islands, i.e. nearest ones in composition (configuration + energetic) space. To that end a number of unbroken bonds must be greater than some critical value. This number has been calculated by a joint integration of interisland spacing and energy barrier distributions using experimentally measured island size and space distributions. At sufficiently high temperatures these calculations predict common thermo activation conductivity as in the case of a random island space distributions, but with activation energy depending on all the morphological parameters of island assembly, including those of spatial correlations. At low temperatures the conductivity S is no longer straightened in Arrhenius coordinates and described by a smooth curve that can be approximated by a simple law $S \sim \exp[-(W/T)^n]$ with fractional exponent n equal to $1/2$ at moderately low temperatures and $n = 1/3$ at very low temperatures as observed in a number of experiments.
 1. V.I. Trofimov, V.A. Osadchenko, Growth and Morphology of Thin Films (in Russian), Moscow. Energoatomizdat, 1993, 272 pp.

12:30

LUNCH

Thursday, June 12, 2003
Jeudi 12 juin 2003

Afternoon
Après-midi

Session IV: Structural nanomaterials from clusters (mechanical, thermal,... properties
Session chair: M. Hou, university Brussels, Belgium

- F-IV.1** 14:00 -Invited- INELASTIC LIGHT SCATTERING: A MULTISCALE CHARACTERIZATION APPROACH TO VIBRATIONAL, STRUCTURAL AND THERMO-MECHANICAL PROPERTIES OF NOSTRUCTURED MATERIALS
C.E. Bottani, **A. Li Bassi**, C. Casari, M. Beghi, INFN - Dipartimento di Ingegneria Nucleare, Politecnico di Milano, Via Ponzio 34/3, 20133 Milano, Italy
Inelastic light scattering is a powerful technique for the characterization of nanostructured materials, at different length scales. Raman scattering is a well established tool for materials characterization (structure, bonding, composition), through the measurement of vibrational properties. Due to phonon confinement, the Raman spectra of nanoparticles and nanostructured materials are substantially different from the spectra of the corresponding bulk, and provide useful information relative to the size and the dynamical behavior of the building blocks. In-situ measurements permit the investigation of phenomena such as cluster deposition, film growth, thermal and chemical stability of nanostructures. Brillouin spectroscopy measures acoustic phonons and elastic properties of thin films and bulk materials at a mesoscopic scale (hundreds of nm). The observation of acoustic damping and localization in nanostructured materials gives access to information such as interaction between nanoscale constituents, phase transitions, self-similar properties and meso-structure dynamical behavior. We provide a wide range of examples: characterization of the elastic properties of cluster-assembled films and ultrathin protective layers; in-situ Raman spectroscopy of metastable linear carbon aggregates (carbynes) produced by cluster beams; measurement of acoustic modes in carbon nanotubes; detection of surface melting of metallic nanoparticles, by detection of confined vibrational modes.
- F-IV.2** 14:40 VIBRATIONS OF AMORPHOUS, NANOMETRIC STRUCTURES: WHEN DOES CLASSICAL CONTINUUM THEORY APPLY?
A. Tanguy, J.P. Wittmer, F. Leonforte, L. Lewis and J.L. Barrat, LPMC, Université Lyon I, France
We study the size dependence of the vibrational eigenmodes of amorphous nanoparticles. We show that classical continuum elasticity (Lamb modes) breaks down when the wavelength of the solicitation is smaller than a characteristic length of approximately 30 molecular sizes. This length is related to the presence of additional vortices in the atomic displacement field of the nanoparticle. These vortices are related to local anisotropy in the inhomogeneous elastic moduli of the amorphous structure. We show how they affect the average mechanical response of the nanoparticles.

Session V: Chemical properties and reactivity of clusters and cluster based nanostructures (catalysis,...)

Session chair: W.D. Schneider, University Lausanne, Switzerland

- F-V.I** 15:00 -Invited- CHEMICAL AND CATALYTIC PROPERTIES OF NANOSCALE, FREE AND SUPPORTED CLUSTERS
Ueli Heiz, **Anke Würz**, Institute of Surface Chemistry and Catalysis, University of Ulm, Germany
The reactivity of nanoscale systems are mainly dominated by quantum-size effects that govern the electronic spectra of clusters, by the structural dynamical fluxionality of clusters, as well as by impurity-doping effects. In this talk these fundamental and unique cluster properties are illustrated by specific examples obtained from molecular beam experiments in the gas phase and experiments on size-selected clusters on surfaces. Where possible, concepts for their understanding are given.
Specifically, the nanoscale reactivity of free, small Ag_n and Au_n clusters will be presented. It will be shown how the interaction and chemical reactivity can be changed with cluster size. On a specific example it will be shown how the reaction mechanism and the energetics of a catalytic cycle can be extracted from the measured, temperature-dependent kinetics. The experimental results are then compared to extensive ab-initio calculations. In a second set of experiments metal atoms and small metal clusters are formed in the gas phase, size-selected and then deposited on thin oxide films grown on metal surfaces. Chemical reactions and catalytic properties on the obtained cluster-assembled materials are then investigated under UHV conditions by means of thermal desorption, infrared spectroscopy and pulsed molecular beams. The oxidation and polymerisation reactions are strongly dependent on cluster size and on the cluster-support interaction, and not only the number of product molecules per cluster is changed, but also the branching ratio of the certain reactions[...]

- F-V.2** 15:40 CHEMICAL REACTIVITY OF NANOCRYSTALS AND CONTROLLING GROWTH OF NANOCRYSTAL ARRAYS
A.I. Klimovskaya, N.N. Grigor'ev, K.N. Grygoryev, Institute of Semiconductor Physics, National Academy of Sciences, Kyiv, Ukraine, T. Kamins, Hewlett-Packard Labs, Palo Alto CA, USA
 Recently striking property of naturally-grown silicon nanocrystals was found. These crystals exhibit high passivity to oxygen. Auger spectra of nanocrystals both as-grown and stored for few years in the atmosphere consist of LVV and KLL peaks characteristic for atomically clean surface. We have analysed theoretically chemical reactivity of nanocrystals and found that a change of the reactivity of nanocrystals as compared with the reactivity of bulk material is a fundamental property of nanoobjects. This opens a way to growing of an array of nanocrystals with a small dispersion of size, shape and physical properties of nanocrystals in array.
- F-V.3** 16:00 CLUSTER-CLUSTER ANNIHILATION WITH SUBSTRATE DIFFUSION-LIMITED MASS TRANSPORT
N.J.A.P. Goncalves(a,c), J.A.M.S. Duarte(b) and A. Cadilhe(a), (a)Centro de Física da Universidade do Minho, 4710-057 Braga, Portugal, (b)Centro de Matemática Aplicada da Universidade do Porto, 4169-007 Porto, Portugal (c)Departamento de Física, Universidade de Trás-os-Montes e Alto Douro, 5000-911 Vila Real, Portugal
 We describe a novel two-species aggregation-annihilation model in which aggregation and annihilation are limited by terrace mass transport. Aggregation takes place due to an effective attractive potential between like species, while annihilation takes place between unlike species upon contact. Contrary to the classic diffusion-limited reactions, the incorporation of an attractive effective potential leads to a much longer time scale for the decay of the concentration. Furthermore, the evolution of our model depends on the flux of particles in the initial pre-deposition stage. We follow the time dependence of the overall number of particles, the number of clusters on the substrate, and the mean cluster size in order to characterize the kinetics. We found a slow, non-mean-field kinetics of the various quantities, in particular of the concentration of particles in the post-deposition evolution. Our model is of interest to people working on heterogeneous catalysis and reactions.
- 16:20 **BREAK**
- 16:30-18:30 **POSTER SESSION II**

Functional nanomaterials from clusters (electronic, optical, magnetic... properties)

- F/PIL.01** THE INFLUENCE OF THE AG BUFFER ON THE STRUCTURAL AND MAGNETIC PROPERTIES IN EPITAXIAL FE FILMS
E. Chemam(a), A. Bouabellou(b), R. Boukhalifa(a), R. Zaidi(a), (a)Institut des sciences exactes et de technologies, Centre universitaire de Tébessa, Algérie (b)Laboratoire des surfaces et interfaces, Université Mentouri de Constantine, Algérie
 The structural and magnetic properties of Ag buffer layer were investigated by x-ray diffraction and magneto-optical Kerr effect (MOKE) measurements. The Fe films, 300Å were deposited by molecular beam epitaxy on single crystal MgO(001) substrates with Ag buffer layer varying from 0 to 150Å. Small and high angle x-ray diffraction confirmed the good layer quality. MOKE hysteresis loops are measured with magnetic field applied along the in-plane <100> and <110> directions of the Fe films at room temperature (RT). The analysis of hysteresis loops indicates an in plane easy magnetization axis and shows the magnetic properties strongly depend on the Ag buffer layer thickness.
- F/PIL.02** RADIOFREQUENCY MAGNETRON CO-SPUTTERING DEPOSITION SYNTHESIS OF CO-BASED NANOCOMPOSITE GLASSES FOR OPTICAL AND MAGNETIC APPLICATIONS
E. Cattaruzza*, G. Battaglin*, P. Canton, F. Gonella*, P. Riello, INFN* and Dipartimento di Chimica Fisica, Università di Venezia, Dorsoduro 2137, 30123 Venezia, Italy
 Transition element nanoclusters embedded in dielectric matrix are important for their optical and magnetic properties. In fact, metal quantum dot composites exhibit an enhanced optical Kerr susceptibility, the most important physical process for applications in all-optical switching devices. Moreover, when materials possessing long-range magnetic order are reduced in size, the magnetic order can be replaced by some other magnetic state. The magnetic properties of nanometer-sized magnetic particles embedded in a dielectric matrix are dominated by the characteristics of the nanoparticle such as the size, the structure, the composition, the surface properties, in terms of both oxidation and anisotropy effects: thus, the definition of flexible preparation protocols able to drive the composite system towards the desired final structure is an important task.
 In this work, Co-doped silica films with cobalt atomic concentration ranging from 0.5 to 10% were synthesized by radiofrequency magnetron co-sputtering deposition technique, for different preparation conditions. In addition, subsequent thermal treatments were performed in oxidizing and/or reducing atmosphere, to promote and control the nanoclusters formation. Structural and optical observations proved the capability to trigger the composite system structure by varying both the deposition parameters and the subsequent annealings: depending on the preparation protocol, cobalt oxides and/or metallic nanoclusters were obtained embedded in silica. In some samples, metallic cobalt nanoparticles with mean size less than 10 nm were revealed to be fcc in structure.

F/PII.03 SUPERCONDUCTING NANOCLUSTERS IN LAYERED STRUCTURES

A.I. Dmitriev, Z.D. Kovalyuk, V.I. Lazorenko, G.V. Lashkarev, A.A. Shtepura, Institute for Problem of Materials Science, National Academy of Sciences of Ukraine, Department for Functional Materials and Cryogenic Investigations, Krzhizhanovskii, 03142 Kiev, Ukraine

The unusual properties of layered crystals InSe intercalated simultaneously by Pb and Li are discussed. Low concentration of Pb is not enough for the formation of continuous metal layers in the interlayer space. Therefore, the magnetoresistivity and electrical properties differ weakly from those for pure InSe. The increase of Pb content results in a qualitative change of these properties. At decreasing the temperature below 7 K one can observe a transition from negative magnetoresistance to positive i.e. from 2D to 3D conductivity. Such a change in the electrophysical properties of InSe intercalated by lead may be explained supposing that Pb in the interlayer space in an amount sufficient to form nanoclusters passes to the superconducting state at $T < 7$ K. The existence of such superconducting islands with dimensions less than 1 μm by XRM studies results in the shunting of a large number of interlayer barriers which is equivalent to the removal of the latter for carriers. Besides that, superconducting cluster of lead cut short the resistance of neighboring layers. All this promotes a decrease of the temperature for 2D to 3D conductivity transition lower than 7 K in comparison with a pure InSe. Simultaneously the critical field of Pb nanoclusters increases to 5.6 T at $T=0$ K due to size effect comparatively to 0.05 T for the bulk state.

F/PII.04 TEMPERATURE EFFECTS ON THE FORMATION OF Si NANOCLUSTERS

Jong Hoon Kim, Kyung Ah Jeon, Jin Back Choi, Chul Woo Oh and Sang Yeol Lee, Department of Electrical and Electronic Engineering, Yonsei University, 134 Shinchondong, Seodaemunku, Seoul 120-749, Korea

Si thin films on p-type (100) Si substrates have been prepared by using pulsed laser deposition (PLD). The optical and structural properties of these films have been investigated as functions of the deposition temperatures and annealing temperatures. Films were deposited from p-type silicon target in He ambient gas pressure of 1 Torr at different deposition temperatures ranging from room temperature to 400°C. After deposition, the silicon thin films were annealed in nitrogen gas at different annealing temperatures ranging from 400°C to 800°C. When the deposition temperature increases, PL intensity abruptly decreases and PL peak shows red shift. As annealing temperature increases, intensity of blue (430 nm) PL increases, on the contrary that of green (580 nm) PL decreases because of decrease of defect centers. These results indicate that the Si nanoclusters were formed by three steps which were growth, defect reducing, and isolation.

F/PII.05 STRUCTURAL AND MAGNETIC PROPERTIES OF Fe-Si-O NANOCOMPOSITES OBTAINED BY SOL-GEL METHODS

D. Predoi, V. Kuncser, G. Schintieie, P. Palade, G. Filoti, National Institute for Physics of Materials, P.O. Box. MG 07, 76900 Bucharest Magurele, Romania and M. Zaharescu, Institute of Physical Chemistry, Romanian Academy, 202 Splaiul Independentei, 77208 Bucharest, Romania and B. Sahoo, W. Keune, Laboratorium für Angewandte Physik, Gerhard-Mercator-Universität, 47048, Duisburg, Germany

The Fe-Si-O nanocomposites obtained a modern sol-gel methods are exhibiting various magnetic, electric and catalytic properties. The SiO₂ matrix was obtained starting from various precursors (methylethoxysilan, phenilethoxysilane and colloidal silica) while for the iron species the precursor was FeSO₄·7H₂O, resulting the samples labeled as MTEOS, PTEOS and S respectively. Therefore different compositions, sizes and related magnetic interactions have been obtained. A sample (labeled as Fe1) prepared in similar conditions but without SiO₂ precursors, was also obtained. The samples were mainly investigated by Mössbauer spectroscopy at low temperatures. An amorphous iron compound with a mean hyperfine field of about 50 T at 5K was present in sample Fe1. Mixed valence iron components were evidenced in the other samples, their relative content and particle size increasing from sample S to sample PTEOS. The blocking temperatures were deduced from Mössbauer spectra recorded at various increasing temperatures.

Structural nanomaterials from clusters (mechanical, thermal,... properties)

F/PII.06 CURVATURE EFFECT IN ULTRA-SMALL SINGLE-WALLED CARBON NANOTUBES

Irene L. Li, Z.M. Li, J.T. Ye and Z.K. Tang, Department of Physics and Institute of Nano Science and Technology, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

Ultra-small single-walled carbon nanotubes (SWNTs) were synthesized in the matrix of AlPO₄-5 zeolite single crystals. Transmission electron microscope (TEM) image shows that the diameter of the SWNTs is as small as 0.4 nm, which is the size of three possible tubes: the zigzag (5,0), armchair (3,3) and chiral (4,2). Three predominant fine structures appeared in the Raman spectrum in the radial-breathing vibration region which correspond to the three different SWNTs. The polarization dependence of the Raman intensity showed that the carbon nanotubes inside the channels of the zeolite are perfectly oriented. Local density functional calculations indicate that when the diameter of the SWNT is very small, strong curvature effects would induce a significant mixing of the unoccupied orbital, which induce interesting novel properties that are not predicted in SWNTs of larger diameter. The Raman results in 0.4nm single-walled carbon nanotubes evinced this curvature effect. The observed frequencies of the radial breathing mode deviated from those predicted by the elastic model due to the curvature effect. There are two features in the Raman spectra: (i) the radial breathing mode frequencies show obvious softening; (ii) the degree of the softening depends on the tube chirality and diameter. The system of the mono-sized SWNTs stabilized in the zeolite channels brings the experimental results much closer to the real of theoretical predictability.

F/PII.07 INDIUM NANOCLUSTERS IN ION-IMPLANTED SILICA: SYNTHESIS AND STABILITY UNDER THERMAL ANNEALING

M.A. Tagliente and L. Tapfer, ENEA, Centro Ricerche Brindisi, SS. 7 Appia 72100 Brindisi, Italy, G. Mattei and P. Mazzoldi, INFN-Dipartimento di Fisica, Università di Padova, via Marzolo 8, 35131 Padova, Italy

Composite materials formed by metal nanoclusters in insulating matrices have been the objects of continuously growing interest due to their peculiar optical, magnetic and catalytic properties. Among the different possible synthesis techniques, ion implantation is very effective to obtain tailored composite materials for the different applications.

In this work, we report on the synthesis of In crystalline nanoparticles by ion implantation of In²⁺ ions (2·10¹⁷ ions/cm², 320 keV) in silica and their thermal evolution by means of in-situ techniques based on x-ray diffraction (XRD) and transmission electron microscopy (TEM). The measurements were carried out in a temperature range between the room temperature and 800°C, which is well beyond the melting point of In (157°C). It is evidenced that the In nanocrystals embedded in the silica matrix exhibit a range of melting temperature between a lower limit corresponding to a slight melting point depression and an upper limit which is higher than the bulk melting point (superheating). After their melting, all the particles remain stable in the form of liquid drops until a threshold temperature of about 800°C, after which they disappear. The exceptional stability of the In inclusions was ascribed to the presence of a thin In₂O₃ shell around the clusters. Below the critical temperature of 800°C, several heating/cooling cycles can be performed in a reproducible way and when the sample is cooled down a remarkable undercooling was observed, indicating the presence of an hysteresis cycle.

F/PII.08 NUMERICAL DETERMINATION OF EFFECTIVE PERMITTIVITY IN COMPOSITE MATERIALS

J. Peon-Fernandez, J. Martin-Herrero, N. Banerji, T.P. Iglesias, Dpto. de Fisica Aplicada, Universidad de Vigo, Lagoas Marcosende, 36200, Spain

The field of composite materials, whose general interest focuses on designing new materials with special extensive magnitudes has been of active research interest. We present here, a simple method for the numerical estimation of the effective permittivity of macroscopically homogeneous, low-loss composite materials constituted of homogeneously mixed two or more suitable components. Although the effective medium theory (EMT), attempts to analytically predict the extensive magnitudes of such systems, the models used fail to incorporate the detailed structural effects in the calculations. This has motivated us to set up a model which can numerically determine the effective permittivity for any general aggregate distribution where the effects of shape, orientation and distribution of the aggregates is easily incorporated. The method is based on the Monte-Carlo random walk iterative calculation of the mesoscopic electric field for a general composite system of clusters distributed within a continuous matrix. We restrict our calculations to the analysis of low loss, non-magnetic systems without free charges. The field distribution in the volume of interest for a quasi-static excitation is solved by simulation, using the fact that the response of the system can be obtained from an analysis of the macroscopic response of a unit cell. We use a further simplification by assuming that the unit cell is equivalent to a new volume with a single cluster, but preserves the average values of the aggregates. Once the detailed structure of the fields is found, we proceed to determine the effective parameters. We present here, the variation of the effective permittivity value with different distributions of spherical clusters within a host matrix.

F/PII.09 ON THE ELECTRIC FIELD DISTRIBUTION IN MACROSCOPICALLY HOMOGENEOUS COMPOSITES

E. Faro(a), J. Peon-Fernandez(b), N. Banerji(b), (a)Dpto. de Matematica Aplicada, (b)Dpto. de Fisica Aplicada, Universidad de Vigo, Lagoas Marcosende 36200, Spain

The study of the electromagnetic response of composite materials requires the determination of the detailed field distribution within its volume. We deal with composites constituted of inclusions embedded in a continuous matrix. Many situations of practical interest could be treated employing a generalised Helmholtz equation for the scalar potential (Coulomb's gauge under the so called Long Wave Approximation (LWA)) where the scattering effects are neglected. The present work deals with the LWA solution for a general problem of field distributions inside such a system under a prescribed potential on its boundary surface. Field equations have been solved by standard methods when subject to the Dirichlet, Neumann or mixed boundary conditions. The problem arises when the boundary potential is unknown on a part of the closed boundary surface which is the real case of interest. The determination of the e.m. response of any homogeneous composite for any external field is carried out by imposing the appropriate forcing potential on the corresponding oriented boundaries, but avoiding any prescription of potentials on the non-oriented boundaries. Many authors have applied the "non reflecting boundary potential" condition on the non-oriented boundaries, a condition that is only a first order approximation and is satisfied only for highly symmetric cluster distributions. In this work we use instead, a periodic Born-Von Karman type potential condition for the lumping potential. The result is a quasi-analytical solution for the field distribution inside the material. From this result, we obtain the effective permittivity and conductivity for a macroscopically homogeneous composites with arbitrary cluster distributions.

Chemical properties and reactivity of clusters and cluster based nanostructures (catalysis,...)

F/PII.10 A QUANTUM MECHANICAL STUDY OF SnO₂ NANOCRYSTALLINE MATERIALS

A.M. Mazzone, C.N.R.-Istituto IMM- Sezione di Bologna, Italy

The purpose of this study is to gain insight into the properties of SnO₂ nanocrystalline materials used for gas sensors. To this purpose, the Hartree-Fock formulation at semi-empirical level, using the Extended Debye-Hückel Approximation, has been applied to the characterization of the electronic charge of realistic grain structures. The grains have the rutile lattice of SnO₂ and, according to experiments, their shape is columnar or spongy with a linear dimension in the range 2 nm. Two types of properties, dealing with the electronic structure of grains and with their absorption capability, respectively, have been considered. In the first case, the parameters investigated are the binding energies, the charge on atoms, the spectrum of allowed energies and vacancies in the oxygen and tin sublattices. These properties are analyzed and discussed in the light of known features of crystalline SnO₂ and of small oxygen and tin clusters. To describe absorption more complex systems formed by the grain and by an adsorbed O₂ and CO molecule have been also considered. These calculations describe preferred adsorption sites, the structure of the deposited molecule and the effects of the adsorbate on the electronic structure of the absorbing medium. Effects arising from the grain size and shape are also discussed.

F/PII.11 STABLE FILMS OF SIZE-SELECTED NOBLE METAL CLUSTERS AS MODEL CATALYSTS

A. Pulisciano, S.J. Park, S. Pratontep, C. Xirouchaki, F. Yin, F. Claeysens, Y. Chen, Q. Guo and R.E. Palmer, Nanoscale Physics Research Laboratory, School of Physics and Astronomy, The University of Birmingham, Edgbaston, Birmingham B15 2TT, U.K.

The deposition of size-selected clusters creates novel surface films. Thus the chemistry of the clusters seems to be fundamentally different from the corresponding single crystal surfaces. In this work we investigate two processes: the stability of pinned size-selected metal clusters at elevated temperatures and the interaction of molecular oxygen with such (Ag) cluster arrays. The metal clusters are produced by an RF magnetron sputtering, gas aggregation cluster beam source, mass selected and deposited on graphite at room temperature. Au⁺ clusters were pinned on the graphite surface in vacuum and subsequently transported into an ultra high vacuum (UHV) Scanning Tunneling Microscope (STM) to investigate the effect of temperature on lateral cluster diffusion in-situ. The pinned clusters appeared to be stable even at temperatures as high as 600 degC; no significant cluster aggregation was observed. For the molecular adsorption experiments, monodispersed Ag⁺ clusters were deposited in UHV on a graphite surface pre-decorated with Ar⁺ defects and investigated by in-situ STM and High Resolution Energy Loss Spectroscopy (HREELS). Measurements of the O₂/Ag/graphite system provide evidence that chemisorbed molecular oxygen (a superoxide-type species) is stabilised at room temperature by these clusters, whereas only atomic oxygen is stable on single crystal Ag surfaces at room temperature. The pinning of metal clusters generates nanostructured surfaces which are stable at room temperature and may act, e.g., as model catalysts.

- F/PII.12** SUPPRESSION OF OVERLAP INTERACTION IN QUANTUM DOT FILMS BY ADSORPTION OF CYANIDE
Shaibal K. Sarkar and Gary Hodes, Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel
 We have recently shown that adsorption of cyanide ion on CdSe and CdS quantum dots increases the localization of charge in the dots resulting in a further increase in bandgap. Closely-spaced quantum dots of very small size can interact due to charge overlap interaction, thereby reducing size quantization in the dots. Here we demonstrate a time-dependent aggregation of CdSe quantum dots in films deposited by chemical solution deposition and show that adsorption of cyanide on these films suppresses the overlap interaction, resulting in bandgaps and optical spectra more typical of isolated dots.
- F/PII.13** CHARACTERIZATION OF THE FIRST TO SECOND ORDER DYNAMICAL PHASE TRANSITION OF THE ZIFF-GULARI-BARSHAD MODEL WITH IMPURITIES
C. Dias and A. Cadilhe, Centro de Física, Universidade do Minho, Braga, Portugal
 We present an extensive Monte Carlo study of a generalized Ziff-Gulari-Barshad model to explain heterogeneous catalysis within the presence of given fraction of impurities. Specifically, we model the steady state of this model for various concentrations of impurities, which can be either constituted of monomers or dimers. We notice, as in previous literature, strong dependence of the dynamic first-order phase transition on the initial fraction of impurity sites. We also characterized the passage from first to second order as one increases the fraction of impurity sites to about 8% of the total surface in terms of the cluster-size distribution cumulants up to the fourth order. We observe a clear, qualitative, crossover of the skewness and of the kurtosis as one passes from the first to the second dynamical phase transition. This work is of relevance to people working on the area of heterogeneous catalysis and reactions.
- F/PII.14** LARGE EFFECTS FROM SMALL SURFACES?
Beatriz Roldán Cuenya, Sung-Hyeon Baeck, Thomas F. Jaramillo and Eric W. McFarland, University of California Santa Barbara, Chemical Engineering Department, 223 Ellwood Beach Dr.12, Goleta, CA 93117, USA
 We are investigating the hypothesis that the size-dependent reactivity of nanoscale metal clusters arises from modifications of their surface electronic structure and not simply from increased surface area compared to continuous films. We have synthesized metal nanoclusters of Au, Pt and Au-Pt alloys supported on titania and silica by utilizing two different methods: (1) thermal evaporation and (2) dip-coating substrates with a monolayer of block co-polymer micelles into which metal salts of nanoscale dimensions are pre-dissolved. The latter technique allows for tight control of mean particle size, size distribution and dispersion. Structural information obtained by AFM, STM, TEM and SEM was used to optimize the synthesis procedure for each oxide support. The size-dependent electronic structure effects were probed by X-ray photoelectron spectroscopy (XPS), and it was found that metal oxidation under atomic oxygen exposure was inhibited for clusters less than 5 nm in diameter. This result suggests the possibility of using these nanoparticles as highly stable oxidation catalysts. The electro-catalytic activity of the clusters will be addressed, and preliminary results shown concerning the oxidation of carbon monoxide by micellar-derived Au clusters and propylene oxidation by thermally evaporated Au islands.
- F/PII.15** CLASSIFICATION OF STRUCTURE OF HYDROGENATED NANOSCALE METALLIC AND COVALENT SYSTEMS (Me, Si, C) FOR THE DEVELOPMENT THE EFFECTIVE METHODS OF THE "CLUSTER CONSTRUCTION" IN THE GASE-PHASE METALLURGY
V.A. Polukhin, L.K. Rigmant, R.M. Belyakova, Institute of Metallurgy of Ural Division of RAS, Amundsen str. 101, Ekaterinburg, Russia
 The complex analysis of theoretical and experimental investigations of nucleation, formation, growth, stability, isomeric transformations and their size-scale (dimensional) dependence under combined temperature and hydrogen treatment of nanostructures (nano-crystalline and nano-scale metallic and covalent Si, C - phases) was in scope using the direct molecular-dynamic simulation (MD-method) and X-ray and electronography methods. The first stage of exploring was concerning with the classification of energies and structure units of nano-scale hydrogenated systems in raw of metal bond weakening (from alkali d-metal to Ge, Si, C)[...] It has been revealed on the basis of MD-simulation results, that in nanoscale limit (for cluster sizes $D=2R$ less than 10 nm) the melt transition started at the temperatures less than these of bulk samples in accordance with 1/R Russanov's low and Tomthson's formalism and included (a) preliminary state of intensive nanostructure isomerisations and (b) intermediate one initiated with virtual liquid film "pocket" formations (with anticipation times about 10-8c) on the surface of nanoclusters through the atom interchange migration and defect formations of "pop-out" types in the surface layers, determined as "quasimelting". So the thin melt films were coexisted thermodynamically with solid-like nanoclusters corners (nuclei). It has been shown that process of Si nanoclusters condensation was realized in two stage: (a) initial one as coalescence of first shell (7 - 9 atoms) and (b) cluster growth itself via the diffusion of absorbed atoms through the surface layer of formed initial clusters.
- F/PII.16** LINEAR NANOSCALE CLUSTERS OF CuI IN Cu-ZSM-5 CATALYSTS
Z.R. Ismagilov, S.A. Yashnik, V.F. Anufrienko, T.V. Larina, N.T. Vasenin, N.N. Bulgakov, S.V. Vosel, L.T. Tsykoza, Boreskov Institute of Catalysis, Prosp. Akad. Lavrentieva 5, 630090 Novosibirsk, Russia
 The catalytic activity of Cu-ZSM-5 depends on level of Cu exchange in zeolite and electron states of copper, oxidation level and coordination [1-3]. The present work deals with EPR and ESDR studies of electron states of copper depending on the method used for preparation of Cu-ZSM-5 (ion exchange, wet impregnation, deposition), basic conditions of synthesis (pH of copper solution, copper precursor, temperature etc.) and copper loading. For calcined Cu-ZSM-5 samples treated in vacuum at 400°C, axial EPR spectra of O^- ion radicals with $g=2.05$ and $g=2.02$, which are presumably assigned to linear $-O^- - Cu^+ - O^- - Cu^+ - O^-$ chains in zeolite channels. We observed a copper state with absorption bands at the unexpected region of 18000 to 23000 cm^{-1} , which relate to the ligand-metal CTB in $-O^- - Cu^{2+} - O^{2-} - Cu^{2+} - O^{2-}$ -like chains in the zeolite channels.
 [1] K.C.C.Kharas, Appl. Catal. B; Environ., 2 (1993) 207
 [2] R.Gopalakrishnan, P.R.Stafford., et al., Appl.Catal. B, 2 (1993) 165
 [3] V.F. Anufrienko, N.N.Bulgakov, Z.R.Ismagilov, et. al. Dokl. RAN 386 (2002) 770 (in Russian)

New trends in theory and computer simulations of cluster structures and properties

- F/PII.17** SURFACE EFFECTS ON STRUCTURAL AND THERMODYNAMIC PROPERTIES OF Cu₃Au NANOCCLUSERS
T. Van Hoof and M. Hou, Physique des Solides Irradiés et des Nanostructures CP234, Université Libre de Bruxelles, Bd du Triomphe, 1050 Brussels, Belgium
Semi-empirical potentials used for atomic scale modeling in metals are known to be poor for modeling low coordination interactions. A popular second moment tight binding potential [1] is revisited on the example of Cu₃Au nanoclusters containing no more than a few hundred atoms. The parameterization of this potential is improved and a coordination correction is presented, based on available empirical data for reduced coordination systems. It is found that a fine-tuning of the parameters for bulk materials allows a significantly better description of the order-disorder transition, as predicted by Metropolis Monte Carlo simulations. Accounting for a coordination correction does not significantly affect the structural and thermodynamic properties of the cluster cores. At equilibrium, cluster cores display the same stability as bulk Cu₃Au and the surface takes over the possible gold segregation.
[1] G.J Ackland and V. Vitek; Phys. Rev. B41, 10324 (1990)
- F/PII.18** SEMIEMPIRICAL CALCULATIONS OF THE COLLECTIVE OPTICAL EXCITATIONS IN SUBSTITUTED OLIGODIACETYLENES
M. Ottonelli, G.F. Musso, D. Comoretto and G. Dellepiane, Università di Genova, Dipartimento di Chimica e Chimica Industriale, Via Dodecaneso 31, 16146 Genova, Italy
We present the results of a series of semiempirical calculations of the electronic and optical excitations of isolated carbazoly-substituted oligodiacetylenes as well as of their small aggregates. We are using the collective electronic oscillator (CEO) approach, based on a time-dependent Hartree-Fock approximation, to analyze the nature of the excitations in terms of the electron-hole pairs distributions generated by photon absorption in neutral and charged systems.
The CEO approach, which uses a semiempirical Hamiltonian, has the advantage of allowing to study each aggregate as a whole molecular system, and consequently to properly take into account interchain screening effects that could heavily modifies the exciton binding energies and the optical gap. The theoretical results will be compared with experimental data obtained for polycarbazolyldiacetylenes.
- F/PII.19** GLOBAL OPTIMIZATION OF SILICON NANOCCLUSERS
L. Chaudhuri(a), S. Sertl(b), Z. Hajnal(a), M. Dellnitz(b), T. Frauenheim(a), (a)University of Paderborn, Department of Physics, Theoretical Physics, Paderborn 33098, Germany (b)University of Paderborn, Department of Mathematics, Paderborn 33098, Germany
We present a new method for the computation of the lowest energy configurations of atomic clusters. It is based on recently developed set oriented numerical algorithms for global optimization of nonlinear functions. Its underlying idea is to combine multilevel subdivision techniques for the computation of fixed points of dynamical systems with well known branch and bound methods. We describe how this method can be used to find global minima of silicon nanoclusters in the SCC-DFTB energy surface. Due to the insufficient experimental evidence of structures of silicon clusters, local minima which are near to the global minimum are also important. By using the above method we were able to calculate such local minima along with the global minimum, too.
- F/PII.20** OSCILLATIONS IN RAMAN SPECTRUM AS DISPLAY OF PHONON SUBBANDS IN QUANTUM-SIZE STRUCTURES
A.M. Yaremko, V.A. Yukhimchuk, E.V. Mozdor, M.Ya. Valakh, Institute of Semiconductor Physics NASU, 03-028 Kiev, Ukraine
Theoretical and experimental study of periodical structure of bands, observed in Raman spectra of Si/Ge and GaAs/AlAs quantum-size structures (QSS) were made. The explanation of such features was done in the framework of developed theoretical approach which takes into account the real crystal structure of both the well and the barrier. The theoretical analysis was made by using the Green function method. It was shown that for study of phonon spectra of QSS it is convenient instead of full Brillouin zone (BZ) (defined by wave vector q , $-\pi/a \leq q \leq \pi/a$, a is a lattice constant) to use the "reduced BZ" (given by wave vector q' , $-\pi/aL \leq q' \leq \pi/aL$, L is a thickness well + barrier). In such description the crystal zones are transformed into sub-zones: i) occurs the folding of dispersion curves at $q = \pi/aL(2n+1)$, ($n=0,1, \dots$); ii) the perturbation, which arises at substitution part (or all) of atoms in chosen unit cells and "creation" of potential well, gives rise to shift of frequencies $\omega_s(q)$ and to lift of some forbidden rules. This "allows" to be observed the bands at $\omega_s(2\pi n/aL)$ forbidden in the ideal crystal. The features noted in i, ii) points take place for both the optical and the acoustic vibrations. The theoretical expressions obtained for the shape of bands were applied to describe the oscillations in the Raman spectrum in the region of acoustic vibrations of Si/Ge and of the optical vibrations of GaAs/AlAs quantum structures.
- F/PII.21** MONTE CARLO SIMULATIONS OF JAMMING COVERAGE OF PRE-TREATED PATTERNED SURFACES
N. Araujo(a), A. Cadilhe(a) and V. Privman(b), (a)Centro de Física, Universidade do Minho, Braga, Portugal, (b)Center for Quantum Device Technology, Clarkson University, New York, USA
We present an extensive Monte Carlo study of the irreversible, competitive deposition of disks of two sizes on a surface with short-range repulsive interactions. In particular, we studied the effect of the substrate patterning on the coverage and on the particle distribution on the surface. We defined parameters, $r<$, $r>$, a , and b as, respectively, the radius of the smaller disks, the radius of the larger disks, the size of square regions of where deposition can take place, and b the distance between such squares on the substrate. We plot a phase diagram characterizing the structure of the jamming state in several limiting cases of interest. We observe regions in the $a/r<$ versus $b/r<$ diagram, with fundamentally different time dependences of the coverage, namely, exponential and power-law approaches to the jamming state. The model, therefore, interpolates between the random, continuum random sequential adsorption, and the regular, lattice like, patterning as we vary the values of $a/r<$ and $b/r<$. We also performed simulations with an initial fraction of dirt already deposited on the substrate. Our study is of interest to people working, for example, in the fields of self-assembled nanostructures, colloids, lithography, and nonequilibrium statistical physics as it provides key parameters and characterization of the evolution towards the jamming state.

- F/PII.22** MONTE CARLO SIMULATION OF THE CDTE LAYERS GROWTH ON THE CdTe(001) AND Si(001) SUBSTRATES
 L. Pyziak(a), I. Stefaniuk(a), I. Virt(b), M. Kuzma(a), (a)Institute of Physics, Rzeszow University, Rejtana 16A, 35-959 Rzeszow, Poland, (b)Institute of Biotechnology, Rzeszow University, Rejtana 16A, 35-959 Rzeszow, Poland
 Very promising method for thin (of nanoscale thickness) AIBVI layer fabrication is pulsed laser deposition method. Using the Monte Carlo procedure the initial stage of the CdTe layer growth on Si (001) and CdTe(001) substrates was simulated. The model for layer growth included: surface diffusion, adsorption and desorption of adatoms, kinetic energy distribution of atoms or ions in the plasma plume and its space and time structure. The shape of the clusters formed depends on these conditions clearly. Layers were obtained for various substrate temperatures. We analyzed morphology and cross-section of the obtained layers. The quality of obtained layers was studied by fractal description. Results of simulations allow to determine the correct choice of layer growth parameters in the real process.
- F/PII.23** DIMENSIONAL COEFFICIENT IN THE PROCESSES OF ISOMERIZATION AND MELTING OF NANOCCLUSERS
E. Potemkina, A. Potemkin, S. Pikalov, V. Polukhin, Institute of Metallurgy of the Ural's Division of Russian Academy of Sciences, Ekaterinburg, Russia
 At the modeling of silicon nanoclusters one should take into account the chemical character as well as the experimental and theoretical data of physical-chemical properties of the silicon states and above all the silicon surface. It is obvious that at the formation of initial structure of silicon nanoclusters one should consider the features of electron structure of the covalent bonds and the dominations for all its solid-phase states. Several models of isomers has been proposed for silicon systems according to the formula $Si(4N+N_c)$ for $N=7,8$ as well as the clusters with a fulleren-like outer coordination shell which consists of $4N$ atoms, and N_c of inner shell. The process of isomerization represents the version of monomolecular reaction and it has been describe by the RRKM theory. It is really important that the melting process doesn't run by means of the weakening of the nanocluster bonds in the solid state but by dint of the fluctuation transition with the further formation of fluid-like or solid-like structure. The interaction of silicon particles one can state by the dependence representing the three-particle potential SW. For $N(r)_\mu$ at the final dimensions of the cluster the junction area is characterized by the final width. In this area the liquid and the solid phases coexist. At the $N>1000$ one might observe the transition of non-crystalline to the crystalline one during the condensation.

Advanced characterization techniques: from individual nanoclusters to cluster assembled nanostructures

- F/PII.24** OBSERVATION OF NANOSTRUCTURE CLUSTER FORMATION OF RARE EARTH IONS IN WIDE BAND GAP FLUORINE DIELECTRIC CRYSTALS USING TRANSMISSION ELECTRON MICROSCOPY WITH ATOMIC RESOLUTION
 G. Drazic, S. Kobe, Jozef Stefan Institute, Jamova 39, 1001 Ljubljana, Slovenia, A.C. Cefalas, E. Sarantopoulou, Z. Kollia, National Hellenic Research Foundation, 48 Vas. Constantinou Avenue, Athens 11635, Greece
 The strong radiative interconfigurational $4f_n-15d(r)4f_n$ transitions of the rare earth (RE) activated ions, in the wide band gap of various fluoride dielectric crystals, can be used for generating coherent VUV or UV light.
 All these applications are depending on the basic physical properties regarding the structure of the levels of the $4f_n-15d$ electronic configuration of the trivalent RE ion and the strength of the interconfigurational $4f_n-15d(r)4f_n$ transitions which greatly depend on clustering of the rare earth ion dopants in the host crystal [1]. In this communication we have applied transmission electron microscopy to investigate the cluster formation of trivalent rare earth ions in different wide band gap dielectric crystals with atomic resolution. Planar features (grain boundaries, defects etc.) and areas with Moire patterns were observed. Single crystalline domains had dimensions of 5nm, and the crystal axis of these domains were slightly tilted relative to each other
 [1] E. Sarantopoulou, Z. Kollia and A. C. Cefalas, V. V. Semashko, R. Yu. Abdulsabirov, A.K. Naumov, S. L. Korableva, "Crystal field splitting of the $4f_{5d}$ electronic configuration of Pr^{3+} ions in wide band gap fluoride dielectric crystals", T. Szczurek, S. Kobe, P. J. McGuinness. Opt. commun.. 2002, vol. 208, pp. 345-358.
- F/PII.25** SAS- X-RAY STUDY OF ULTRADISPERSED METAL OXIDES IMPREGNATED INTO THE SiO_2 POROUS MATRICES
M.E. Boiko, Ioffe Physical-Technical Institute, Saint Petersburg, Russia, V.N. Beger, State Institute of Fine Mechanics and Optics (Technical University)
 There is the great interest paying to magnetically ordered nanostructures due to problems of the magnetic state with the lowered dimension and supermagnetism. This special class of such systems is represented by materials have been synthesized in a porous medium forming nanosize clusters.
 Several types of nanostructured materials based on oxides of cobalt and bismuth in silicate porous glasses were manufactured and investigated. Samples contain up to 5-7% cobalt and bismuth. SAXS-investigations were performed. Sizes and dispersions of nanoclusters of Co and Bi oxides were measured (as well as sizes of pores). It has been discovered that clusters of oxides of Co and Bi involve the space of a great number of pores. The type of distribution and dimension of these clusters are discussed.
- F/PII.26** SMALL-ANGLE SCATTERING OF X-RAYS - NEW WAY OF NANO - CRYSTAL SEMICONDUCTORS CHARACTERIZATION
M.E. Boiko, A.M. Boiko, A.S. Sakov, Ioffe Physical-Technical Institute of RAS, St Petersburg, Russia
 Characterization techniques of nanostructures is in continuous expansion.
 I regret to say that there are no perfect single crystals as synthetic as nature. Dopants, defects of crystal matrix distributed in volume of crystal in any order or chaotic. Optoelectronic properties of all kinds of crystal depend on crystal structure and superstructure law of such distribution. One of the major driving forces for materials development over the past few decades has been the materials displaying good mechanical and optoelectronic properties. In the invention of the devices based Si and SiC we concerned with the problem of bulk crystal and substrate characterization. The aim of our paper is comparing superstructure of porous silicon carbide grown up in various processes and forecasting substrate influence on SiC formation. In the first time we used Small-Angle Scattering of X-rays (SASX) for studying superstructure phenomena in single crystals and films. The field of superstructure dimensions was in range up to ~ 1000 nm. We compare superlattice and cluster measurement data of porous Si obtained in various circumstances with SASX and comparing SASX data with two-crystal diffractometry and X-ray adsorption porosity measurement. The type of distribution and dimension of these superlattices, porous, clusters are discussed. We propose mathematics models of those distributions.

F/PII.27 AFM AND MICRO-RAMAN INVESTIGATION ON FILTERS COATED WITH SILVER COLLOIDAL NANOPARTICLES
Maurizio Muniz-Miranda and Massimo Innocenti, Dipartimento di Chimica, Università di Firenze, Via della Lastruccia 3, 50019 Sesto Fiorentino, Italy

Ag-coated surfaces are obtained by filtration of silver colloidal suspensions through aluminium oxide membranes. This technique leads to a deposited layer of nanostructured metal, which ensures an efficient SERS (Surface Enhanced Raman Scattering) effect. Varying the volume of the aqueous colloidal suspension to be filtered can change the thickness of the silver layer. As detected by AFM (Atomic Force Microscopy), the surface is formed by spherical or ellipsoidal silver particles with 30 nm as average diameter. These particles can form some isolated bumps higher than 200 nm. The micro-Raman investigation is here coupled with the AFM measurements to analyse the surface morphology by evaluating the SERS enhancement of an organic ligand. The adsorption of ligand is obtained by filtering a diluted ethanol solution of p-nitrobenzoic acid through the Ag-coated filters, which are successively washed with pure ethanol. This procedure allows leaving onto the substrate only the ligand really adsorbed on silver. The SERS signal results strongly enhanced when the laser beam is focalised on the prominent metal bumps.

Friday, June 13, 2003
Vendredi 13 juin 2003

Morning
Matin

Session VI: New trends in theory and computer simulations of cluster structures and properties

Session chair: A. Andriotis, FORTH, Heraklion, Greece

- F-VI.1** 8:50 -Invited- **AB INITIO STUDY OF NANOMATERIALS: FROM GROWTH MECHANISMS TO ELECTRONIC PROPERTIES**
Xavier Blase, CNRS and Laboratoire de Physique de la Matière Condensée et Nanostructures (LPMCN), Université Claude Bernard, Lyon, France
We study on the basis of ab initio simulations the properties of various systems of nanometric size. We will first discuss the growth mechanisms of pure and doped carbon nanotubes [1] by using Car-Parrinello molecular dynamics simulations. We will then describe the original properties of the silicon clathrates, a novel phase built of face-sharing Si₂₀, Si₂₄ and Si₂₈ clusters. The influence of doping on the electronic properties will be presented [2]. Finally, from a methodology point of view, the problems encountered by the well known Density Functional Theory (DFT) for the description of the electronic properties of nanostructured materials will be exemplified. A more accurate quasiparticle approach will be presented for the study of the electronic properties and tunneling currents of surfaces and adsorbed molecular systems [3].
[1] Blase, Charlier, De Vita, Car et al, Phys. Rev. Lett. 83, 5078 (1999).
[2] Connétable, Timoshevskii, Artacho, Blase, Phys. Rev. Lett. 87, 206405 (2001).
[3] Rignanese, Blase, Louie, Phys. Rev. Lett. 86, 2110 (2001).
- F-VI.2** 9:30 **STABILITY OF HYDROGENATED NANODIAMONDS AND THE GROWTH OF DIAMOND FILMS: AN AB INITIO MOLECULAR DYNAMICS STUDY**
Jean-Yves Raty (a,b) and Giulia Galli(b), (a)University of Liege, Belgium, (b) Lawrence Livermore National Laboratory, California, USA
During the recent years, nanosized diamonds have been discovered in a large variety of environments. From detonation soots to CVD deposited films, chondrites meteorites and even comets, the nanoparticles have similar size distributions. We perform a ab initio molecular dynamics simulations to obtain the structures of hydrogenated nanodiamonds up to 1.6 nanometers in diameter (447 atoms), with different hydrogen surface coverages. For each nanoparticle size, the stability is addressed via a chemical potential approach. As a function of the hydrogen chemical potential, the nanoparticles surface undergo progressive reconstruction up to the totally bare and reconstructed 'bucky diamond' structure [1]. We show that the difference in formation energy between the stable hydrogenated nanodiamond and the bare structure decreases with the particles diameter, the crossover occurring between 2 and 3 nanometers. The comparison with a similar chemical potential study of diamond surfaces indicates that the nanodiamonds will either a) remain as is and form isolated particles or ultrananocrystalline diamond films, or b) coalesce into larger particles and form microcrystalline diamond films, depending on the hydrogen chemical potential.
This work was performed under the auspices of the U.S. Department of Energy at the University of California/Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48. [1] To appear in Phys. Rev. Letters
- F-VI.3** 9:50 **FIRST - PRINCIPLES SIMULATIONS OF 2D Cu SUPERLATTICES ON MgO**
Yuri F. Zhukovskii(a), Eugene A. Kotomin(a), David Fuks(b), **Simon Dorfman**(c), A. Marshall Stoneham(d), Oleg Sychev(e) and Gunnar Borstel(e), (a)Institute of Solid State Physics, University of Latvia, Kengaraga 8, 1063 Riga, Latvia, (b)Materials Engineering Department, Ben-Gurion University of the Negev, POB 653, Beer-Sheva, Israel, (c)Department of Physics, Israel Institute of Technology - Technion, 32000 Haifa, Israel, (d)Center for Materials Science, Dept. of Physics and Astronomy, University College London, Gower str., London WC1E 6BT, U.K., (e)Fachbereich Physik, Universitaet Osnabrueck, Barbarastrasse 7, 49069 Osnabrueck, Germany
There is an increasing demand for high quality epitaxially grown copper films on nonconducting substrates used in integrated circuits. One of the important issues is the fabrication of smooth Cu films on modified MgO substrates, to serve as a growth template for device structures, such as tunneling magnetoresistance devices (TMR). The copper/magnesia interface is also of great importance for other technological applications, including catalysis, metal-matrix composites, recording media, etc. DFT calculations of the 2D Cu superlattices on MgO were carried out with the CRYSTAL98 code. We consider a model of an initial stage of the Cu/MgO(001) interface formation with 1/4 sub-monolayer and monolayer (ML) substrate coverages by Cu and compare our results with various experimental and theoretical data, in order to clarify the nature of the interfacial bonding. One general conclusion to be drawn from our simulations is that there is no strong ionic bonding on the perfect Cu/MgO(001) interface. In the case of 1/4 Cu ML a direct interaction between polarized Cu adatom and external O²⁻ ion is more preferable than the interaction between Cu and Mg²⁺ (0.62 and 0.48 eV per adatom, respectively). For 1 Cu ML, when adatoms are positioned over oxygen ions, the adhesion energy is enhanced by the interaction of Mg²⁺ ions with the substrate-induced electron density accumulated in the interatomic positions of metallic adsorbate.

F-VI.4 10:10

STRUCTURAL AND ELECTRONIC PROPERTIES OF SMALL Cu_m (m=3-6) CLUSTERS

Y. Pouillon(a,b) and C. Massobrio(a), (a)IPCMS, 23 rue du Loess BP 43, 67034 Strasbourg Cedex 2, France, (b)ENEA Calcolo e Modellistica, C.R. Casaccia SP103, 00100 Rome A.D., Italy

The bonding between copper and oxygen atoms and its evolution with size has motivated extensive photoelectron spectroscopy measurements (see H. Wu, S. Desai and L.-S. Wang, J. Phys. Chem. A, 101, 2103 (1997)). Despite the small sizes involved in the experimental work carried out so far, the structure of the isomers is far from being elucidated. To go beyond qualitative interpretations, we have performed structural optimizations by using the first-principles molecular dynamics framework. The calculations on copper oxide clusters presented here are carried out within density functional theory, with a plane-wave basis set and generalized gradient corrections. Our results show that except in one case the CuO₃ cluster takes a planar geometry, one of these isomers being an ozonide. The most stable isomer of CuO₄ also exhibits planar geometry. Results obtained for CuO₆ show that the symmetries deduced from the experiments do not correspond to the most stable forms, and are even unstable in some cases. More generally, the three largest clusters in the series are made of the structural blocks corresponding to the shape of the smaller isomers. Ozonides are favoured as the number of atoms increases.

10:30

BREAK

Session VII: Advanced characterization techniques: from individual nanoclusters to cluster assembled nanostructures

Session chair: K. H. Meiwess-Broer, university Rostock, Germany

F-VII.1 11:00 -Invited-

SYNCHROTRON RADIATION TECHNIQUES FOR STRUCTURAL AND MORPHOLOGICAL INVESTIGATIONS ON CLUSTERS: PRESENT AND FUTURE

F. d'Acapito, ESRF, Grenoble, France

Third generation synchrotron radiation sources provide extremely brilliant hard x-ray beams that have recently open new ways for the investigation of cluster matter. Grazing incidence geometry is widely used because, providing a probe beam confined in a thin surface layer, permits experiments of X-ray Diffraction or Small Angle Scattering for the characterization from a structural or morphological point of view of nanoparticles deposited on surfaces. By using this technique, O. Robach et al (Phys. Rev. B 60, 5858) have determined the shape and strain state of Ag particles on MgO grown in situ, for coverages from 0.2 to 6 monolayers. Another noticeable example, is the determination of the strain and composition fields in InAs quantum dots deposited on GaAs (I. Kegel et al. Phys. Rev. Lett. 85, 1694).

By exploiting the intense beams it is also possible to collect x-ray absorption data on diluted systems like in the work of G. Faraci et al (Phys. Rev. Lett. 86, 3566) where the presence of Co dimers in Ag was evidenced or to record diffraction data in times in the ps regime for pump-and probe experiments like the study (A. Plech et al. ESRF Highlights 2002) of the temporal evolution of the thermal expansion of Ag particles in glass heated by a short (80 ps) laser pulse.

The ultra-bright and coherent beams from 4th generation x-ray sources like Free Electron Lasers (FEL) in the hard x-ray regime are foreseen to permit the structural analysis on single molecules (R. Neutze et al. Nature 406, 752). First data from soft x-ray FELs are already present in literature like the studies on multiply ionized Xe clusters (H. Wabnitz et al. Nature 420, 482).

F-VII.2 11:40

EXTRAORDINARY HALL EFFECT (EHE) AND X-RAY PHOTOEMISSION (XPS) STUDIES OF TWO DIMENSIONAL FILMS OF MAGNETIC CLUSTERS

J. Tuaille-Combes(a), O. Boisron(a), G. Guiraud(a), A. Gerber(b), A. Milner(b), P. Melinon(a), A. Perez(a), (a)Laboratoire de Physique de la Matière Condensée et Nanostructures, Université Claude Bernard, 43 Bd du 11/11/1918, 69622 Villeurbanne Cedex, France, (b)Raymond and Beverly Sackler Faculty of Exact Sciences, School of Physics and Astronomy, Tel Aviv University, Ramat Aviv, 69978 Tel Aviv, Israel

The low Energy Cluster Beam Deposition technique (LECBD) is used to prepare nanostructured thin films from clusters preformed in the gas phase. Supersonic beams of pure (Co, Ag, Pt) or mixed clusters (CoSm, CoAg, CoPt) are prepared in a laser vaporisation source (Ti-Sapphire or Nd-YAG laser) and deposited at room temperature in an UHV-chamber. We produce films of isolated supported clusters as well as clusters embedded in matrix, obtained from conventional atomic evaporation. The goal of this study is to realise array of high magnetic anisotropy clusters. These arrays are obtained by cluster deposition onto patterned graphite (Focus Ion Beam technique). To characterise our two dimensional (2D) magnetic Co-clusters films, we use the Extraordinary Hall Effect technique. We will present results obtain from films composed by 0.01 equivalent nm to 1 equivalent nm of Co-clusters embedded in Pt-matrix. To obtain a high blocking temperature (only 30 K for nanometric Co-clusters) we study mixed clusters SmCo, CoAg, CoPt. The first results of in-situ X-ray photoemission (XPS) on CoAg and CoPt mixed cluster thin films (0.1 nm to 2 nm) will be exposed. We observe an evolution of the binding energy peaks of Co and Ag (resp. Pt) various the CoAg (resp. CoPt) clusters thickness.

L. Bardotti et al. Applied surface science 191 (2002) 205.

A. Gerber et al. JMMM 241 (2002) 340-344.

M. Négrier et al. Europ. Phys. J. D9 (2000) 475.

F-VII.3 12:00

ATOMIC-MESOSCOPIC SCALE TRANSITION OF DIAMOND-LIKE METAL-CARBON COMPOSITES STUDIED BY OPTICAL SECOND HARMONIC GENERATION

T.V. Murzina, R.V. Kapra, O.A. Aktsipetrov, Physics Department, Moscow State University, 119992 Moscow, Russia, V.F. Dorfman, Atomic-Scale Design, Incorporated, PO Box 210483, San Francisco CA 94121, USA

In this paper we introduce the experimental results of atomic-mesoscopic scale transition of diamond-like metal-carbon composites studied by optical second harmonic generation (SHG) technique. The samples studied are 1 μ m thick carbon films doped by such metals as Cu, Ag, Pt, Pd, Hf, Mn, Cr and W in a wide range of concentrations. The SHG probe is used because of its high sensitivity to electronic and morphological properties of surfaces, interfaces and nanostructures. In our studies, the SHG technique allowed to distinguish between cluster-like and amorphous structure of carbon-metal composites. In particular, an increase of the SHG response is observed as metallic clusters are formed in the films under the thermal annealing for {Pt|C} and {Pd|C} ASC films. This is a manifestation of atomic-mesoscopic scale transition for these structures. It is demonstrated that the dependence of the SHG intensity on resistivity of films draws near the nucleation curve in these films. At the same time, a wide range of atomic-scale composite films is estimated which retains a stable amorphous structure in a wide range of resistivity.

It is demonstrated that the SHG reflected from the films is diffuse and depolarized, which is connected with the structural inhomogeneity of the films and allows to describe the nonlinear optical response of the films in terms of hyper-Rayleigh scattering.

F-VII.4 12:20

SIZE AND NUCLEATION BEHAVIOUR OF GOLD CLUSTERS ON KBr(001) CHARACTERIZED BY DYNAMIC SFM AND TEM

C. Barth and C. Henry, CRMC2-CNRS, Campus de Luminy, case 913, 13288 Marseille, France

Our major interest concerns the catalysis of nano sized gold clusters on oxide surfaces which we characterize with different kinds of surface analysis tools. Despite several investigations of gold clusters which had a size of several tens of nanometers, we recently analysed the size and the nucleation behaviour of clusters with only a size of few nanometers at surface defects on KBr(001) with dynamic Scanning Force Microscopy (SFM) and Transmission Electron Microscopy (TEM). The (001) surface of KBr has been chosen due to its easy preparation by cleavage in UHV and due to the access to atomic resolution imaging SFM.

In the contribution we present results of two different samples: On the surface of the first KBr crystal we deposited gold with a nominal thickness of 1.0 ML, on the surface of the second crystal a much smaller amount of gold with a nominal thickness of 0.1 ML. First measurements have been taken with the force microscope, after several series of experiments we dismantled both crystals from the UHV chamber and imaged them with the electron microscope. The measurements show that the clusters have a size of only a few nanometers and that they preferentially nucleate at steps and dislocation loops. A detailed description of the size and the nucleation behaviour with respect to the deposited amount of gold will be given. Further on, a comparison will outline the advantages and disadvantages of the two applied techniques.

12:40-13:00

Concluding remarks