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E-MRS Spring Meeting 2002
June 18 - 21, 2002

SYMPOSIUM A

Atomic Scale Materials Design

Symposium Organizers:

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Papers will be published in Computational Materials Science

E-MRS 2002 SPRING MEETING

SYMPOSIUM A

Tuesday, June 18, 2002
Mardi 18 juin 2002

Morning
Matin

Session I: General

- 09:00 **A-I.1** **LARGE SCALE SIMULATIONS WITH QUANTUM MECHANICAL FORCES**
Rodney J. Bartlett, Carlos Taylor, Marshall Cory, Piotr Rozyczko and Keith Runge Quantum Theory Project, University of Florida, Gainesville FL 32611, USA
Our goal is predictive simulations for materials. To achieve this, we introduce a simplified (transfer) Hamiltonian based upon coupled-cluster theory which can encode accurate quantum mechanical forces in a way that permits large scale MD to be performed in a multi-scale simulation, with up to ~1000 quantum mechanical atoms. We demonstrate different behavior under stress when using QM forces compared to classical ones for selected prototypes silica systems. This work is supported by the US National Science Foundation, Materials Sciences Division.
- 09:40 **A-I.2** **ACCELERATED MOLECULAR DYNAMICS METHODS**
Arthur F. Voter, Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA
A significant problem in the atomistic simulation of materials is the time scale limitation of the molecular dynamics method. While molecular dynamics can easily access nanoseconds with empirical potentials, many of the most interesting diffusive events occur on time scales of microseconds and longer. If the transition state (i.e., the saddle point) for a given reaction pathway is known, transition state theory can be applied to compute a rate constant directly. If all possible events are known for a given system, these rate constants can be employed in a kinetic Monte Carlo algorithm to evolve the system from state to state over long time scales. Unfortunately, for realistic systems, the transition states are often hard to find. Moreover, it is often the case that our intuition about how the system will behave breaks down, so that key events are missing from the kinetic Monte Carlo treatment. This situation is typical in metallic surface growth, where complicated exchange events prevail, and in many other physically important processes, such as annealing after radiation damage, or diffusion at a grain boundary.
- 10:20 **BREAK**
- 10:40 **A-I.3** **MECHANICAL PROPERTIES AND THE CHEMICAL BOND**
Ruben Perez, Departamento de Fisica Teorica de la Materia Condensada, Universidad Autonoma de Madrid, Spain
The importance of a proper description, using quantum mechanics, of the atomic events that are ultimately responsible for the mechanical properties of materials is emphasized. Traditional approaches, based on classical potentials, failed to capture, in cases like brittle fracture, even the qualitative behaviour found in the experiments. However, it is nowadays possible to design and perform first-principles total energy calculations that reveal fundamental aspects of the microscopic origin of the observed macroscopic mechanical behaviour. These ideas are illustrated with applications to:
*Atomic Force Microscopy (AFM), where the simulations provide the basis for the interpretation of the atomic contrast observed in non-contact Frequency-Modulation AFM experiments[1], and the resolution limits in contact AFM[2].
*Brittle fracture in silicon[3].
*Diamond polishing, with particular attention to the origin of the significant anisotropy in the experimental wear rates[4].
[1] M. Lantz et al, Science 291, 2580 (2001).
[2] M. R. Jarvis, R. Perez and M. C. Payne, Phys. Rev. Lett. 86, 1207 (2001).
[3] R. Perez and P. Gumbsch, Phys. Rev. Lett. 84, 5347 (2000); Acta mater 48, 4517 (2000).
[4] M. R. Jarvis, R. Perez and M. C. Payne, Phys. Rev. Lett. 80, 3428 (1998).

Symposium A

- 11:20 **A-I.4** **COMBINED ELECTRONIC STRUCTURE AND EVOLUTIONARY SEARCH APPROACH TO MATERIALS DESIGN**
Thomas Bligaard, Gisli Johannesson, Andrei Ruban, Hans Skriver, Karsten Jacobsen and Jens Norskov, Center of Atomic-scale Materials Physics, Department of Physics, Technical University of Denmark, Lyngby, Denmark
We describe the use of an evolutionary algorithm in conjunction with density functional theory to optimize material properties. The approach is illustrated by the search for the most stable four component alloys that can be constructed from 32 different metal elements in the periodic table. We immediately obtain well-known high-temperature super alloys like Ni₃Al. The method also predicts that several other three and four component alloys should be equally stable and thus potentially interesting as high temperature alloys.
- 11:40 **A-I.5** **ARE DFT LEVEL CALCULATIONS THE ANSWER TO REAL-WORLD MOLECULAR SYSTEMS?**
Robert J. Meier, DSM Research, P.O.Box 18, 6160 MD Geleen, The Netherlands
This contribution is intended to initiate discussion on the performance of first principles calculations for molecular systems. Since quantum mechanics was formulated, we have seen significant development in both theory as well as application. Lack of computing power has long limited application to many practical, real-world, systems. Compared to a decade ago, however, it is now possible to study molecular species of a size that is becoming relevant for both the academic as well as for the industrial chemist. But how good are the numbers we generate using such, nowadays almost exclusively, DFT calculations?
Whereas hybrid methods such as B3LYP often show good compromise between accuracy and computational cost compared to, e.g., MP2, in some important cases the DFT approach does not yield appropriate results, sometimes even leading to unreliable answers. In this talk this will be illustrated. We will discriminate between what we will call accuracy and reliability.
In addition, throughput of calculations is a real bottleneck. What we need are quantum computational methods providing us with reliable (relative) energies, for systems up to say a hundred atoms. Such calculations should be possible on a routine basis. We plead for a set of benchmark systems to evaluate newly introduced functionals, and mutually compare performance of existing methods.
- 12:00 **LUNCH**

Symposium A

Tuesday, June 18, 2002
Mardi 18 juin 2002

Afternoon
Après-midi

Session II: Semiconductors

- 14:00 **A-II.1** **MULTISCALE MODELING OF DEFECT KINETICS IN SEMICONDUCTORS**
R.M. Nieminen, COMP/Laboratory of Physics, Helsinki University of Technology, P.O. Box 1100, 02015 HUT, Finland
The interplay between non-equilibrium defects, impurities and dopants is crucial for the behavior of semiconductor structures upon processing and annealing. We combine atomistic calculations for the energetics and structures of defect complexes with rate equation, kinetic Monte Carlo, and cellular automaton simulations of long time and length scale phenomena. As specific applications, we discuss oxygen clustering in silicon, anisotropic chemical etching of silicon surfaces, and self-diffusion in gallium antimonide.
- 14:40 **A-II.2** **SUBSTITUTIONAL N-TYPE DOPING OF DIAMOND**
Karin Larsson, Department of Materials Chemistry, Angstrom Laboratory, University of Uppsala, Uppsala, Sweden
One of the major topics in diamond science and technology today is the search for a suitable donor impurity in diamond which can be introduced into the diamond lattice and which has a donor level close enough to the conduction band minimum. A substitutional n-type doping of diamond during CVD growth has been studied in the present investigation. This incorporation mode depends on both the kinetics of the growth process and the solubility of the impurity. Kinetic trapping may then be possible although the final n-type doped product is thermodynamically very unfavourable. Calculations have in the present study been carried out for N, P and S impurities using the DFT and Hartree-Fock levels of theory. The effect of i) chemisorption of hydrogenated impurity species and the following substitutional incorporation into the ii) upper surface atomic layer and iii) bulk position, on materials properties like thermodynamics, solubilities, geometrical structures and electronic structures, have been of a special interest to study more thoroughly.
The results in the present investigation clearly show that the trend in diamond (111) surface reactivity towards N(or P or S)-containing gaseous species, does generally not follow the corresponding trend in solubility. However, the N impurity have the largest solubility and the surface shows the most pronounced surface reactivity towards the NH_x species (X=0-3).
- 15:00 **A-II.3** **THERMAL TRANSPORT ACROSS SiC/METAL INTERFACES AND CONTACTS**
Eleni Ziambaras and Per Hylgaard, Department of Applied Physics, Chalmers University of Technology and Goteborg University, 41296 Goteborg, Sweden
The SiC/metal contacts and interfaces are heterostructured materials and can inhibit thermal transport even though both SiC and metals are excellent thermal conductors. The semiconducting nature of SiC limits the interface thermal transport to phonons. Such phonon transport can suffer both dramatic scattering and total-internal reflection effects [Phys. Rev. B 56, 10754 (1997)]. The intended use of SiC for high-power semiconducting devices motivates a larger investigation of consequences for the thermal stability of SiC contacts --- can we make robust soldering? Here we present calculations of both the SiC/Al-interface structure and thermal transport. We model the interface atomic relaxation and dynamics and use a Boltzmann-equation approach to study the phonon transport. We document important thermal-conductivity reductions arising from the significant difference in material hardness (total-internal reflection effects) at the SiC/Al interface and we initiate the study of phonon scattering and transport in SiC/metal contacts.
Research funded by EU project ATOMCAD and by the Swedish Foundation for Strategic Research (SSF) through ATOMICS.
- 15:20 **A-II.4** **FIRST PRINCIPLES DETERMINATION OF HIGH EFFICIENCY NEW PHOTOVOLTAIC MATERIALS**
P. Wahnou, P. Palacios and C. Tablero, ETSI Telecomunicacion, Universidad Politecnica de Madrid, 28040 Madrid, Spain
The aim of this work is to investigate within a DFT quantum mechanical framework the possibilities of a new material, with improved optoelectronic properties, in order to produce a new photovoltaic device with a significant increment of the theoretical limiting efficiency of conventional solar cells. To reach that, we study at atomic level, the characteristics of a new photovoltaic semiconductor material with an isolated metallic intermediate band located in the semiconductor energy band gap. Our final purpose is to determine the potential for photovoltaic conversion of this structure by establishing its limiting efficiency.
In a previous work, using an accurate First Principles method we proposed an alloy semiconductor containing Ti atoms, of the type: TiGa_mX_n with X=As or P, that presents an isolated half filled intermediate band.
Our purpose here is, to present this kind of band diagram characteristics and phonon dispersion studies for several alloys compounds. For this work, we use the ab-initio Siesta code based on density functional techniques. In such a method the exchange and correlation energy is calculated in the LDA and GGA approximations. The Siesta code builds up the force constant matrix needed to determine the phonon dispersion diagram. A preliminary limiting efficiency of 46% has been found in some of these compounds using a procedure of calculation developed in a previous work.
- 15:40 **BREAK**

Session III: Spin Systems

- 16:00 **A-III.1** **SELF-COMPENSATION IN FERROMAGNETIC SEMICONDUCTORS**
Steven C. Erwin, Center for Computational Materials Science, Naval Research Laboratory, Washington DC, USA
Ferromagnetism in Mn-doped GaAs is generally believed to be mediated by holes arising from substitutional Mn. Measured hole concentrations are much smaller than expected from simple electron counting, for unknown reasons. We present theoretical evidence that the source of this compensation is interstitial Mn. We show that under non-equilibrium conditions characteristic of the low temperatures used during growth, interstitial Mn can be formed by a simple low-energy surface adsorption process. In the bulk, interstitial Mn plays a dual role: as a source of hole compensation, and as a source of localized spins whose interactions are mediated by electrons. We develop a mean-field theory of magnetism that self-consistently accounts for both substitutional and interstitial Mn as well as their mutual compensation.
- 16:40 **A-III.2** **ELECTRONIC PROPERTIES OF Mn-COMPOUNDS UNDER STRAIN**
A. Debernardi, M. Peressi and A. Baldereschi, Istituto Nazionale per la Fisica della Materia (INFN), Trieste, Italy
The recent discovery of giant magneto-resistance has driven increasing interest to the study of magnetic materials. The main target is the design and the realization of new devices with materials whose magnetic properties could be tailored in accordance to the needs of electronic industry. Within the solid state community is rapidly becoming popular the word "spintronic" to denote electronic-like heterostructures where the relevant physical quantity is the spin of the carriers and its interactions with external magnetic fields rather than the charge of holes and electrons and the associated electronic properties. In this context the most promising materials are Mn compounds, grown on different semiconductor substrates. A recent experiment has proved the possibility to grow ordered films (heterostructures) of MnAs on ZnSe. The presence of a ZnSe buffer layer exclusively stabilizes a particular phase ("type-B") of MnAs; at variance, the coexistence of different phases in the magnetic epitaxial layers is experimentally observed when the substrate is GaAs. Due to lattice mismatch the Mn-compound epilayer display a deformed structure with respect to the bulk one, i.e. the structure is strained. We present first-principles calculation of electronic structure of Mn-based compounds under strain. Our calculation is done within the framework of density functional theory by using the plane wave pseudopotential method.
- 17:00 **A-III.3** **FIRST PRINCIPLE STUDY OF ELECTRONIC STRUCTURE AND TOPOGRAPHY OF ADSORBED METALLIC QUANTUM DOTS**
T. Torsti, Laboratory of Physics, Helsinki University of Technology, P.O. Box 1100, 02015 HUT, Finland, **V. Lindberg**, Dept. of Physics, School of Mathematics and Systems Engineering, Växjö University, 35252 Växjö, Sweden, M.J. Puska, Laboratory of Physics, Helsinki University of Technology, P.O. Box 1100, 02015 HUT, Finland and B. Hellsing, Dept. of Physics, Chalmers University of Technology, 412 96 Göteborg, Sweden
We have modeled a one monolayer (ML) thick Na quantum dot (QD) on a Na covered Cu(111) surface, with focus on the electronic structure and real space topography. The surface electron states are obtained by substituting the Na layer by jellium with parameters close to those used for bulk Na metal. The influence of the Cu(111) substrate is taken into account by introducing a layer of less dense jellium below the Na layer. The QD's are assumed to be cylindrical in shape. The calculations are based on the Density functional theory applying the MIKA (Multigrid Instead of the K-space) real-space multigrid method.
To fit the parameters we have studied a free standing Na ML and 1 and 2 ML Na on Cu(111), and compared with theoretical and experimental results. As a reference we have also studied a 1 and 2 ML thick free standing cylindrical QD. The system of a one ML Na QD adsorbed on a substrate formed by one complete Na ML on Cu(111) is carefully studied. The MIKA package provides us with the possibility to perform calculations on large systems with thousands of electrons and to accurately calculate the wavefunctions in regions of low valence electron density. The local density of states (LDOS) are calculated and compared with differential conductance (dI/dV) spectra and constant current topographs from Scanning Tunneling Microscopy.

Wednesday, June 19, 2002
Mercredi 19 juin 2002Afternoon
Après-midi

Session IV: Nano Technology

- 14:00 **A-IV.1** **MAGNETISM OF MONOATOMIC WIRES ON VICINAL SURFACES**
D. Spisák, Institut für Materialphysik, Universität Wien, Sensengasse 8/12, 1090 Wien, Austria
There are three key steps in the development of one-dimensional nanostructures: fabrication, characterization and application. In our contribution we concentrate on the second step, characterization of the structure and magnetic behaviour of monoatomic wires grown on Cu and Ag surfaces with a high density of steps from the theoretical point of view.
At first, the geometry of clean Cu(11 \bar{n}) and Cu(10 \bar{n}) vicinal surfaces is optimized by means of calculated interatomic forces, and the formation energies of steps along the {110} and {100} direction are compared with experimental estimates. In the following, the monoatomic Fe wires are placed at various positions onto Cu substrate. The preferential positions of wires are predicted to be the inner corner sites of the steps. From the total energy differences between ferromagnetic and antiferromagnetic configurations the effective intrawire and interwire magnetic coupling constants are estimated. In all investigated cases the resulting magnetic order is ferromagnetic. Regarding an array of wires as a quasi-2D XY ferromagnet we find the Curie temperature of the system using Monte Carlo simulation.
Finally, a possibility of magnetism in monoatomic wires made of 5th and 6th row elements, which are nonmagnetic in bulky structure, is explored and discussed. The obtained results are in complete agreement with the known trends that a reduced dimensionality promotes magnetism.
- 14:40 **A-IV.2** **AB INITIO MODELLING OF MOLECULAR ELECTRONICS DEVICES**
Mads Brandbyge(a), Jeremy Taylor(a), Jose-Luis Mozos(b), Pablo Ordejon(b) and **Kurt Stokbro**(a), (a)Mikroelektronik Centret, Technical University of Denmark, 2800 Lyngby, Denmark, (b)Institut de Ciencia de Materials de Barcelona, CSIC Campus de la U.A.B., Spain
I will present our newly developed method, TranSIESTA[1,2], which enables a full atomistic description of nanosized electronics devices under operation conditions. The method is based on density functional theory, and uses local basis sets[3] combined with a non-equilibrium Greens function transport scheme. With this package it is possible to calculate the selfconsistent electronic structure, electrical current, and current induced forces of a nanostructure coupled to 3-dimensional electrodes with different electrochemical potentials, using a full atomistic ab initio description of the entire electrode and the nanostructure.
One of the most popular methods to couple molecular devices to external electrodes is via thiolate bonds. One of the key characteristics of such a device is the corresponding contact resistance, however, different experiments seem to give conflicting results for the inherent resistance of a thiol bond. I will present theoretical results for the IV characteristics of different organic molecules coupled to gold electrodes via thiolate bonds and compare with the corresponding experimental data. In several experiments the molecules have an asymmetric coupling to the external electrodes and I will show how this asymmetry may lead to rectification in the device[4].
[1] M. Brandbyge, K. Stokbro, J. Taylor, J. L. Mazes, P. Ordejon, Material Research Society symposium proceedings volume 636, D9.25 (2000).
[2] M. Brandbyge, K. Stokbro, J. Taylor, J. L. Mazes, P. Ordejon, condmat 0110650
[3] SIESTA: D. Sanchez-Portal, P. Ordejon, E. Artacho and J. Soler, Int. J. Quantum Chem. 65, 453 (1997).
[4] J. Taylor, M. Brandbyge, and K. Stokbro. Submitted.
- 15:20 **A-IV.3** **AN ACCURATE THEORETICAL APPROACH FOR ELECTRON TRANSPORTATION PROPERTIES OF SINGLE MOLECULAR DEVICES**
Yi Luo, Theoretical Chemistry, Department of Biotechnology, Royal Institute of Technology, SCFAB, 10691 Stockholm, Sweden
We have developed a new theoretical approach to characterize the electron transportation process in molecular devices based on the elastic-scattering Green's function theory in connection with the hybrid density functional theory without using any fitting parameters. Two molecular devices with benzene-1,4-dithiol and octanedithiol molecules embedded between two gold electrodes have been studied. The calculated current-voltage characteristics are in very good agreement with existing experimental results reported by Reed et. al for benzene-1,4-dithiol [Science, 278(1997) 252] and by Cui et al. for octanedithiol [Science, 294(2001) 571]. Our approach is very straightforward and can apply to quite large systems. Most importantly, it provides a reliable way to design and optimize molecular devices theoretically, thereby avoiding extremely difficult, time consuming laboratory tests.
- 15:40 **BREAK**
- 16:00-18:00 **POSTER SESSION I**

- A/PI.01** A FOURFOLD COORDINATED POINT DEFEC IN SILICON
Stefan Goedecker, Thierry Deutsch, Luc Billard, CEA-Grenoble, DRFMC/SP2M, 17 avenue des Martyrs, 38054 Grenoble Cedex 9, France
Due to their technological importance, point defects in silicon are among the best studied physical systems. The experimental examination of point defects buried in bulk is difficult and evidence for the various defects usually indirect. Simulations of defects in silicon have been performed at various levels of sophistication ranging from fast force fields to accurate density functional calculations. The generally accepted viewpoint from all these studies is that vacancies and self interstitials are the basic point defects in silicon. We challenge this point of view by presenting density functional calculations that show that there is a new fourfold coordinated point defect in silicon that is lower in energy.
- A/PI.02** A THEORETICAL INVESTIGATION OF ADSORPTION ENERGIES TO A (110)-CRYSTAL SURFACE OF c-BN USING A DFT APPROACH
I. Arvidsson and K. Larsson, The Angstrom Laboratory, Department of Materials Chemistry Box 538, 751 21 Uppsala, Sweden
Cubic boron nitride has a wide field of applications due to its extraordinary physical and chemical properties. When using vapour deposition techniques such as ALD, the grown films usually become a mixture of various phases like c-BN, hexagonal BN and amorphous BN. To be able to optimize the growth of c-BN using thin film layer techniques, it is of highest importance to achieve a better understanding of the different reaction mechanisms that are occurring at the surface during the deposition.
Therefore, various adsorption processes involving a (110)-crystal surface of cubic BN has in the present work been investigated theoretically using a DFT approach. A three dimensional slab model was used to simulate the surface. In addition, several test calculations were made to ensure the accuracy of the model. In order to prevent a collapse of the upper surface atoms (from a cubic to a hexagonal structure) surface-terminating species have to be induced in the model. This work focuses on H as a most promising saturating species. Its adsorption energy has been calculated to both a surface boron and nitrogen atom. Furthermore, adsorption processes of several gaseous boron and nitrogen hydrides have also been induced in the present study. The results shows that H is a good terminating specie, and that BH_x and NH_x adsorb rather strongly if they are attached to an atom of a different kind.
- A/PI.03** ATOMIC SIZE OF IRRADIATED ADVANCED MATERIALS EVALUTION
I. Kh. Abdukadirova, Institute of Nuclear Physics Academy of Science of Uzbekistan. 702132, Tashkent, Ulugbek
The optical, mechanical and dielectrical properties of some advanced dielectrics materials for opto- and microelectronics crystals corundum and quartz irradiation by neutrons are investigated, a comparison is made with the properties of the samples before irradiation. On the basis of measurements of these characteristics the value of microparameters polarizability before and after irradiation a samples was calculated. Using these data dose dependence of these microcharacteristics polarizability of crystals was evaluated. It was established that a noticeable the variation of atomic and electronic undersystems of crystals may take place a dose at which a rapid phase transition occurs in quartz. Using these data of polarisability, we also evaluated from the Braun formula a value of atomic size for both crystals (a1 and a2). Analysis of the dose dependence a1(F) and a2(F) is found that reveals radiation stability atomic size of studied crystals at high irradiation doses (? 1021 cm⁻²) in a channels of the reactor. The experimental dependence of atomic size for irradiated dielectrics materials is of especial interest in theoretical aspects at the atomic scale materials design.
- A/PI.04** ATOMIC DYNAMICS OF CLUSTERS OF THE SOLIDIFIED INERT GASES
S.B. Feodosyev, I.A. Gospodarev, E.S. Syrkin, Institute for Low Temperature Physics and Engineering, NASU, Lenin ave. 47, Kharkov 61103, Ukraine and O.V. Gryshayev, Physics-Technology Department, National Technical University, "Kharkov Polytechnical Institute" 21 Frunze str., 61002 Kharkov, Ukraine
Theoretical study of atomic dynamics for the inert gas cluster of different sizes (from 13 atoms) both free and impurity distributed in the bulk or at crystal surface was carried out at microscopic scale. The vibration spectra and mean square displacements are calculated for differently situated atoms of such systems.
In particular, it is shown that isotropic cluster (i.e. of that, which grows by means of uniform enough filling of the coordination spheres), beginning from the size of 500-600 atoms (i.e. filling of 19-20 coordination spheres), the mean square displacements of the outer and inner atoms are practically similar to the same characteristics of the flat surface, or, respectively, near the interface. Due to that, the peculiarities of atom dynamics in the cluster of irregular shape are similar to the corresponding peculiarities, which were studied earlier for the atoms adsorbed at the crystal surface [1].
The dynamics of isolated vacancy in the FCC-crystal lattice was examined and contribution of vacancies into the additive thermodynamical properties was analyzed. Atomic dynamics near the micropores is studied. The later are considered as vacancy cluster.
[1] A.M.Kosevich, A.Mayer, S.B.Feodosyev, I.A.Gospodarev, V.I.Grishaev, E.S.Syrkin, Atom dynamics of micro-clusters on atomically smooth surfaces, Superlattices and Microstructures, v.27, (2000) pp. 7-14.
- A/PI.05** NUMERICAL ESTIMATION OF THE PULLING RATE AND MELT TEMPERATURE RANGES IN THE CASE OF THIN FILAMENT GROWN BY E.F.G. METHOD
L. Braescu, Politehnica University Timisoara, P-ta Regina Maria no.1, 1900 Timisoara, România, A.M. Balint and St. Balint, University of the West Timisoara, Blv. Pärvan no.4, 1900 Timisoara, România
In this paper we find the range of the pulling rate and melt temperature couples for which the system of differential equations, which governs the evolution of the crystal radius r and the meniscus height h in the case of thin silicon filaments, grown from the melt in a vacuum by E.F.G. method, has asymptotically stable steady states. Computation is made in a nonlinear model for a die of radius r₀=2 [cm x 10⁻²] in two cases: the meniscus weight is ignored (H₁) and the meniscus weight is considered (H₂), respectively.
We find also the asymptotically stable steady states and we estimate the region of attraction of each steady state. Using these regions of attraction we give a model based simulation of the growth process when during the growth the pulling rate v and the melt temperature T_m at the meniscus basis change.
We compare the results obtained in the cases (H₁) and (H₂), respectively

- A/PL06** OPTIMIZATION OF EFFICIENT ATOMIC CHARGES MODELS FOR MATERIALS DESIGN
Didier Mathieu, Eric Germaineau, CEA - Le Ripault, BP 16, 37260 Monts, France
With regard to materials design, many properties of interest depend on interatomic interactions. The electrostatic term is often significant. For complex materials - especially organics - involved in real-life applications, the charge distribution is described in term of discrete populations on atoms, that may be used either for force-field simulations or QSPR predictions. Whenever extended systems are considered, atomic charges cannot be derived from quantum wavefunctions. The electronegativity equalization principle provides efficient alternative models, but the significance of the values thus obtained is somewhat ambiguous. Therefore, a non-selfconsistent scheme including screening is parameterized to mimic Mulliken, Hirschfeld or potential-derived atomic charges. The latter are especially tedious to reproduce accurately, in contrast to Mulliken charges. This suggests a new parameterization against EL charges. As they stand, present models have been successfully applied to the prediction of fluid densities, sublimation enthalpies and reactivity.
- A/PL07** ATOMIC SCALE SIMULATION OF THE STRESS RELIEF IN TETRAHEDRAL AMORPHOUS CARBON
A.Yu. Belov, Forschungszentrum Rossendorf e.V., Institute of Ion Beam Physics and Materials Research, P.O. Box 510119, 01314 Dresden, Germany
Tetrahedral amorphous carbon (ta-C) is an amorphous form of carbon with a high content of sp³ bonded atoms, which can be deposited as thin films by energetic carbon ions or neutral atoms. As-grown ta-C films possess a high level of intrinsic compressive stresses (~10 GPa) inhibiting the use of this very promising material. The stress is due to a specific growth mechanism (subplantation), resulting from a competition between the densification of subsurface layers by incoming ions and the thermally activated diffusion of subplanted atoms to the surface. In agreement with experiment, we demonstrate using atomic scale simulation that low-temperature annealing can induce a considerable stress reduction in as-grown ta-C with minor changes in its atomic structure and density. Simulating annealing by means of empirical molecular-dynamics with the interatomic Brenner potential for carbon and realistic boundary conditions, the dependence of the residual stress on the annealing temperature was investigated. It is found that a complete stress relief in ta-C is not accompanied by a change in the short-range order. The average atomic coordination remains nearly constant up to 1400 K. The stress relaxation mechanism discussed involves only structural optimization within the sp³ bonded constituent of ta-C and does not require clustering of sp² bonded atoms.
- A/PL08** ON THE OPTICAL BOWING CALCULATION AND THE QUANTITATIVE ESTIMATION OF THE DIFFERENT CONTRIBUTIONS TO DISORDER: APPLICATION TO ZnCdSe ALLOY
Ali Zaoui, Max-Planck-Institut für Metallforschung, Seestr. 92, 70174 Stuttgart, Germany
We Present an ab initio pseudopotential study based on a direct supercell approach to investigate the disorder effects on the optical band-gap in ZnCdSe alloy system. The disorder parameter (bowing) is detailed and explained from the well known approach of Zunger and co-workers. A comparison is also made with the virtual crystal approximation (VCA). We show that the nature of the bowing can be easily seen from a simple analysis based on a direct supercell calculation. For the alloy studied in this work, we found a main contribution from the volume deformation effect, while the chemical charge transfert as well as the relaxation effects have a smaller contribution.
- A/PL09** THE PRESSURE EFFECT ON ELECTRONIC PROPERTIES OF II-VI COMPOUNDS BY SEMI-EMPIRICAL TIGHT-BINDING METHOD
Y. Al-Douri, Computational Materials Science Laboratory, University of Sidi Bel-Abbès, PO Box 89, Sidi Bel-Abbès, Algeria
A semi-empirical tight-binding sp³s* method for tetrahedral co-ordinated cubic materials is used and applied to ZnSe and ZnTe to present the electronic band structures. The ionicity factor under effect of pressure is presented by means of a recent model. The structural phase transition can be seen from the behaviour of the bonding character. The results are compared with the theoretical and experimental data are in reasonable agreement.
- A/PL10** THE DOPANT DISTRIBUTION IN SEMICONDUCTOR CRYSTALS, GROWN IN A BRIDGMAN-STOCKBARGER SYSTEM, COMPUTED IN THE MODIFIED CHANG-BROWN MODEL
M.M. Mihailovici, A.M. Balint, St. Balint, University of the West Timisoara, Blv. Pârvan no.4, 1900 Timisoara, România
In this paper we consider the modified Chang-Brown model which takes into account the unsteady thermo-convection in the melt, the decrease of the melt in the ampoule, the rejection at the interface and a particular morphology of the solidified front, i.e. the precrystallization-zone[1]. This zone is considered to be a thin porous layer, of width 10⁻⁹ m, masking the crystal, in which there are periodically distributed solid inclusions of size 10⁻¹⁰ m. In this layer, the dopant diffusivity is reduced from D to D_{eff} = D×0.917, the heat conductivity is increased from K to K_{eff} = K×1.1 and the flow is not influenced[2]. We give a model based simulation of the axisymmetric flow, heat transport and dopant dispersion evolution in the melt and we compute the dopant distribution in a Ga-doped Ge semiconductor crystal grown in terrestrial conditions.
[1]M.M Mihailovici, A.M. Balint, St. Balint; ICCG 13, Kyoto, Japan, 30.07-4.08.2001 (to appear in J. Crystal Growth)
[2]A.M. Balint, M.M. Mihailovici, D.G. Baltean, St. Balint; J. Crystal Growth 230/1-2 (2001) 195.
- A/PL11** FOURTH-ORDER REAL SPACE ALGORITHM FOR SOLVING LOCAL SCHROEDINGER EQUATIONS AND NEW SCF ACCELERATION TECHNIQUES
Auer Jakob, E. Krotscheck, Institut fuer Theoretische Physik, JKU Linz, 4040 Linz, Austria, Siu A. Chin, Departement of Physics, Texas A&M University, College Station TX 77843, USA
We describe a rapidly converging algorithm for solving the Schrödinger equation with local potentials in real space. The algorithm is based on solving the Schrödinger equation in imaginary time by factorizing the evolution operator to fourth order with purely positive coefficients. When compared to the existing second order split operator method, our algorithm is at least a factor of 100 more efficient. We also present efficient Newton methods to solve the selfconsistency cycle of the Kohn-Sham equations used in Density Functional theory.

- A/PI.12** ENERGETIC CALCULATIONS OF DIFFERENT DEFECTS IN GaN USING A MODIFIED EMPIRICAL POTENTIAL
J. Kioseoglou(a), H.M. Polatoglou(a), L. Lymparakis(b,a), G. Nouet(c) and Ph. Komninou(a), (a)Aristotle University of Thessaloniki, Department of Physics, Solid State Section, 540 06 Thessaloniki, Greece, (b)Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin-Dahlem, Germany, (c)ESCTM - CRISMAT, UMR 6508 CNRS, ISMRA, 6 Boul. Marechal Juin, 14050 Caen Cedex, France
GaN is a wide-gap III-V semiconductor ($E_g=3.4\text{eV}$ at room temperature) which has recently established as a promising material for optoelectronic application. GaN-based devices may contain high densities of defects such as threading dislocations, planar defects and nanopipes, which can reach 10^{10}cm^{-2} , and it is clear that an improvement in the crystalline quality of the layers would allow higher performance of the devices. There been some attempts to obtain an empirical potential but none of them is very satisfactory till now. In order to achieve a realistic description of the microscopic structure and the energetic configuration of the defects, a large number of atoms are taken in account. Since we need two different atoms in order to represent the GaN structure and due to the different chemistry environment for each of them, the atomistic modeling of defects is very demanding and a properly established empirical potential is a necessity. We choose the Stillinger-Weber potential as the base and we adjust the parameters in Ga-Ga, N-N and Ga-N bonds using ab-initio and experimental results from the literature or by employing new. The input data comprises of the different crystalline phases of Ga, N₂ and of GaN. A fair description is obtaining for all the cases and better for GaN. We test the potential by calculating previously studied planar defects. Using it we study planar defects which have currently a high interest and are observed experimentally.
- A/PI.13** ATOMIC SCALE SIMULATION OF VIBRATIONAL PROPERTIES OF SiGe/Si ISLANDS
H. Kassem, M. Djafari Rouhani, G. Landa, J. Groenen, Laboratoire de Physique des Solides, Université Paul Sabatier, Toulouse, France, J. Dalla Torre, CEA, Saclay, France
A large number of recent works have been devoted to the study of the growth of Ge and Ge-Si alloys on (001)Si substrates. The reason is the potentiality of this structure in microelectronic and optoelectronic devices such as quantum dots. In particular, the formation of regular Ge-Si islands embedded in Si matrices is a promising technique for the fabrication of quantum dots for optoelectronic applications. The second reason is more fundamental and is related to the prototype nature of this structure which involves two elemental semiconductor materials with perfect covalent bonding, both having cubic diamond crystal structures.
Our objective is to use the Kinetic Monte Carlo technique to reproduce the main features of the growth of Si-Ge alloys on (001)Si substrates, on the basis of our previous calculations on the heteroepitaxial growth of compound semiconductors.
In this paper, we will report on preliminary results of the above investigation, concerning mainly the effect of shape and local composition of the islands on the vibrational properties of the system, in particular relation to Raman Spectroscopy data. The case of large pyramidal islands presenting (311) facets, on the free (001)Si surface or embedded in an Si matrix, with various non uniform composition inside the islands will be presented. The calculated Raman spectra will be compared to experimental results obtained by Micro-Raman Spectroscopy.
- A/PI.14** A THEORETICAL STUDY OF DOPANTS ACTIVATION IN CO-IMPLANTED (N AND P) SiC
Riccardo Rurahi(a,b), Eduardo Hernandez(b), Philippe Godignon(a), Pablo Ordejon(b) and José Rebollo(a), (a)Centre Nacional de Microelectronica, (CNM - CSIC), Barcelona, Spain, (b)Insitut de Ciencia de Materials de Barcelona, (ICAMB - CSIC), Barcelona, Spain
For its outstanding performances in high temperature and high contamination environment, especially when submitted to high frequency operations, silicon carbide (SiC) is one of the most promising wide band-gap semiconductors that could replace silicon in a relatively large field of applications.
Understanding the details of the doping process and modeling it on the atomic scale will be one of the most powerful tool to fill the gap with silicon-based technology and to make competing device fabrication feasible.
Recently the co-implantation of two popular n-type dopants, like N and P, has become an interesting issue in the perspective of increasing the activation rate. Experiments gave results which are encouraging and at the same time puzzling.
Few basic mechanisms which pay an important role in the co-implantation of N and P in SiC have been studied theoretically by accurate DFT calculations using the SIESTA code, in the attempt to get a better insight to the atomic interactions that rule this process.
- A/PI.15** A NOVEL SCHEME FOR CALCULATIONS OF ELECTRICAL PROPERTIES OF MOS STRUCTURES
E.A. Burovski and I.Ya. Polishchuk, Kinetic Technologies, pl. Kurchatova 1, Moscow 123182, Russia, Kurchatov Institute Russian Research Center, pl. Kurchatova 1, Moscow, 123182 Russia
A prediction of the electrical properties of MOSFET devices is of high importance especially in view of the search for novel high-k replacements of the conventional SiO₂ gate dielectric. We have developed a simple semi-analytical scheme, allowing one to calculate the leakage I-V characteristics through the ultra-thin dielectric films, as well as the overall MOSFET C-V characteristics. The technique involves two steps. At the first step the calculation of the electronic states and the corresponding charge distribution in the inversion layer of the substrate is performed using the uniform WKB approximation (that allows us to avoid an explicit solution of Schrodingeris and Poissonis equations) and an Ansatz for the electrostatic potential. At the second step, the tunneling processes are taken into account. At present, all the calculations are done in the network of the ideal film model. The results obtained in the network of the ideal film model are in a good agreement with other model calculations available in the literature. A comparison with the experiments allows one to extract contributions from different leakage mechanisms induced by the non-ideality of the film (e.g. defects, impurities, SILC).

- A/PL16** ATOMISTIC STUDY OF ION BEAM DEPOSITION CONDITIONS FOR HARD AMORPHOUS CARBON
A.Yu. Belov and H.U. Jaeger, Forschungszentrum Rossendorf e.V., Institute of Ion Beam Physics and Materials Research, P.O. Box 510119, 01314 Dresden, Germany
The influence of deposition conditions on the sp³ content, intrinsic stress, and elastic modulus in hard amorphous carbon (a-C) films was studied at the atomic scale. Simulation of ion beam deposition of carbon films was performed by the molecular-dynamics method with a modified analytical hydrocarbon potential of Brenner. Deposition of films with a thickness of up to 10 nm was computed for ion energies E = 10-80 eV, and for substrate temperatures ranging from 100 to 900 K. The dependence of the sp³ content and the intrinsic stress on substrate temperature was found to be in qualitative agreement with experiment. At low substrate temperatures and low ion energies, the sp³ fraction increases with ion energy, giving at E > 30 eV a highly sp³ bonded tetrahedral amorphous carbon (ta-C) with a high level of intrinsic compressive stress. This trend also remains at room temperature, however with lower values of sp³ content, whereas at T > 200°C a transition to graphite-like a-C with dominating sp² bonding was found.
- A/PL17** FUNDAMENTAL STUDY ON "PHONON-BAND ENGINEERING" TO DESIGN ARTIFICIAL MATERIALS FOR NEMS
K. Hayashi, H. Kojima, H. Konno, Advanced Materials Science R&D Center, Kanazawa Institute of Technology, 3-1, Yatsukaho, Matto, Ishikawa 924-0838, Japan
In order to develop methods of designing artificial materials of desired tribological characteristics for nano-electromechanical systems (NEMS), a better atomistic understanding of energy-dissipation mechanism is indispensable. We explored law of wearless friction accompanying steady sliding motion between mesoscopic lattices by numerical simulations using simplified two- and one-dimensional models in previous studies, where we found that unlike the wearless-frictional characteristics of a macroscopic solid system those of an isolated mesoscopic system reflect phonon modes of the lattices sliding relative to each other. These studies suggested possibility of designing artificial materials of desired frictional characteristics for sub-micrometer size mechanisms and actuators by "phonon-band engineering" utilizing nano-fabrication technology.
In the present study, molecular dynamics simulations using sheet-doped models were carried out to analyze systematic change in the frictional characteristics due to the isotope substitution [1]. Based on these analyses we discussed how the resonant peaks appeared in the sliding velocity dependence of the frictional force are associated with the local density of phonon states (DOPS) around the interface of harmonic lattices approximating the MD simulation model, taking account of shift and broadening of the peaks due to anharmonicity of the interatomic potential.
[1] K. Hayashi et al., Computer Physics Communications, 142/1-3 (2002) 238.
- A/PL18** THEORETICAL STUDY OF ALKYL DERIVATIVE C₃₇H₅₀N₄O₄ MOLECULE FOR STABLE MOLECULAR RECTIFIER: GEOMETRIC AND ELECTRONIC STRUCTURES Hiroshi Mizuseki, Kenji Niimura, Chiranjib Majumder and Yoshiyuki Kawazoe Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
Recently, the molecular electronics has attracted strong attention as a "post-silicone technology" to establish a future nanoscale electronic devices. To realize this molecular device, unimolecular rectifying function is one of the most important constituents in nanotechnology [C. Majumder, H. Mizuseki, and Y. Kawazoe, Molecular Scale Rectifier: Theoretical Study, J. Phys. Chem. A, 105 (2001) 9454-9459.]. In the present study, the geometric and electronic structure of alkyl derivative C₃₇H₅₀N₄O₄ (PNX) molecule, (donor - spacer - acceptor), a leading candidate of molecular rectifying device, has been investigated theoretically using ab initio quantum mechanical calculation. The results suggest that in such donor-acceptor molecular complexes, while the lowest unoccupied orbital concentrates on the acceptor subunit, the highest occupied molecular orbital is localized on the donor subunit. The approximate potential differences for optimized PNX molecule have been estimated at the HF/6-31g++(d,p) level of theory, which achieves quite good agreement with experimentally reported results.
- A/PL19** FARADAY SCREENING OF ELECTRIC FIELDS IN BUCKMINSTERFULLERENE ENDOHEDRALLY DOPED WITH LITHIUM
P. Delaney, L. Tong and J.C. Greer, NMRC, University College, Cork, Ireland
The trapping of an atom in the interior of buckminsterfullerene is referred to as endohedral doping; we study the endohedral doping of buckminsterfullerene with lithium, denoted as Li@C₆₀. We consider the energetics of lithium within the fullerene cage, and in particular investigate the manipulation of the endohedral lithium by external electric fields having magnitudes typical of scanning tunneling microscopy (STM) experiments. The lithium atom is effectively ionized within C₆₀, transferring its sole valence charge to the carbon cage. We show that at low values of external electric field that the C₆₀ anion acts as an effective Faraday cage, screening the lithium cation trapped within the molecule. At higher values of electric field, the cage is sufficiently polarized allowing the lithium cation to interact with the external field, and thus the endohedral dopant's position can be manipulated by the orientation and magnitude of the external field.
- A/PL20** STRUCTURAL, MECHANICAL, AND THEIRAL PROPERTEIS OF COPPER NANOWIRES
Jeong Won Kang, Won Ha Moon and Ho Jung Hwang, Semiconductor Process and Device Laboratory, Department of Electronic Engineering, Chung-Ang University, 221 HukSuk-Dong, DongJak-Ku, Seoul 156-756, Korea
We have investigated the cylindrical and the pentagonal multi-shell copper nanowires using classical molecular dynamics simulations and a many-body potential function of the second-moment approximation of tight-binding scheme. The stable structures of the ultra-thin multi-shell nanorods and nanowires have only the hexagonal surface lattice composed of coaxial cylindrical shells with {111}-like surfaces. Semi-classical orbits in a circle and circular rolling of a triangular network could explain the structures of the cylindrical ultra-thin multi-shell copper nanowires. A calculation of the angular correlation function and the radial distribution function for nanowires showed that the structural properties of nanowires became closer to those of the bulk with increasing nanowire diameter. We have also investigated the pentagonal multi-shell copper nanorods and nanowires, composed of a central atomic strand and polygonal tubes. The structural properties of the pentagonal multi-shell nanorods and nanowires, which have the square surface lattice and diameters of several nanometers, are close to those of fcc as the sub-units composed of both a triangular and a quadrangular pyramids oriented in the <100> directions. The decagonal multi-shell nanowires are another structure related to the pentagonal multi-shell nanowires.

- A/PI.21** MONTE-CARLO SIMULATION OF ELECTRON CONDUCTANCE AND MAGNETORESISTANCE IN MAGNETIC POLARON SYSTEMS
J.-M. Liu, Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China, Laboratory of Laser Technologies, Huazhong University of Science and Technology, Wuhan 430074, China, K.F. Wang, X.H. Zhou, G.L. Yuan, Y. Yang and Z.G. Liu, Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China
A simple model is proposed to calculate the electron conductivity, magnetoresistance in phase separated magnetic polaron systems and a Monte-Carlo algorithm based on this model is developed. Our simulation predicts clear insulating-metallic transition upon decreasing of temperature and the one-to-one correspondence between this transition and the ferromagnetic transition in the system. This paper will present a detailed description of the simulated results.
- A/PI.22** PROPERTIES OF SINGLE-WALL NANOTUBES: FULL-POTENTIAL LCAO CALCULATIONS
Ruth Pachter, Brahim Akdim and Xiaofeng Duan, Air Force Research Laboratory, Materials & Manufacturing Directorate AFRL/MLPJ, 3005 P St. Bldg. 651, Wright-Patterson AFB, OH 45433-7702, USA
In our continuing efforts to study the properties of single-wall nanotube materials (SWNTs), we present a full potential LCAO DFT study of structural, mechanical, electronic, and optical properties of C(n,n) and C(n,0) [n=(4,6,8,10)] SWNTs, as isolated tubes, or as crystalline-ropes, optimizing the intertube distance, as well as comparative results for boron nitride tubes. Structural and mechanical properties generally agree well with previous theoretical and experimental work, and moreover, our detailed study provides insight into specific structural aspects, for example, we note a different trend in bond lengths of armchair and zigzag tubules. An upshift in the Raman radial breathing mode due to intertube coupling is calculated and compared to experiment. The effects of intertube coupling on the band-gap of semiconducting tubes, and the opening of a pseudo-gap in the band structure of metallic tubes, are also discussed, as is a detailed comparison to BN tubes. These calculations provided the basis for the computational approach we used for our study of the effects of water adsorbates, protonation and finite length of SWNTs.
- A/PI.23** SIZE-/ORIENTATION-CONTROLLED ELECTRONIC AND MECHANICAL PROPERTIES OF SILICON NANOWIRES: A FIRST-PRINCIPLES STUDY
Y. Kong and H. Gao, Max-Planck-Institut fuer Metallforschung, Seestr. 92, 70174 Stuttgart, Germany
A great deal of interest in functionalized semiconductor nanowires has been stimulated by recent demonstration that doped Si nanowires functionalized with organic and biological molecules may be used to create highly sensitive, electrically based nanosensors for biological and chemical species. Applying DFT-based real-space electronic structure method, in the present study, we calculate electronic and mechanical properties ab initio for ideal [111]-, [110]- and [112]-oriented Si nanowires with different size. The structure of Si nanowire and its atomic basis vectors are fully relaxed in our calculation. On the basis of calculated results, size and orientation dependence of the electronic structure and mechanical quantities, such as equilibrium geometry, theoretical strength and Young's modulus, are investigated and compared with available experimental results. In addition, Simple theoretical model is applied to discuss the doping effect by either electron or hole.
- A/PI.24** POSSIBILITY OF THE CHARGE CONTROL OF THE FORMATION OF THE MOLECULAR AND ATOMIC CLUSTERS
V.A. Lykakh, National State University "KPI", Frunze str.21, Kharkov 61002, Ukraine and E.S. Syrkin, Institute for Low Temperature Physics & Engineering NASU Lenin ave. 47, Kharkov, 61103, Ukraine
It is theoretically investigated the conditions of formation of clusters and their superlattice stimulated by charge carriers. The ions or more movable charge carriers is known to form the ordered structures at the surface of dielectric or semiconductor. These charge ordered structures usually have too perfect triangle lattice with easy control of parameters for charge carriers by external voltage. The charge ordered structures can also be defected by control way if we create artificial mechanical defects or electrodes on the surface.
The cluster growth demands the charge ordered structures with intercharge distance much more then sizes of the atoms or molecules using for cluster creating. After the charge ordered structures preparing on the surface we can began the process of the atomic or molecular condensation. Each particle on the surface feels the effect of inhomogeneous electric fields of the charge centers, ponderomotor forces move the condensed molecules diffusion on the substrate surface in the direction of the charge.
The original cluster position and internal structure is determined by charge position and charge-molecule interaction. The fixation of the cluster parameters needs the decreasing of the substrate temperature after the cluster formation and then decreasing voltage to zero and disappearing of the charge carriers. Then internal structure of the clusters change under only intermolecule and molecule-substrate interactions.
- A/PI.25** QUANTUM TOPOLOGICAL APPROACH TO ATOMIC SCALE MATERIALS DESIGN
S.A. Beznosyuk, Altai State University, Lenin Street 61, 656099 Barnaul, Russia
According to quantum topological approach there is hierarchy of three main levels of materials design. First of them is atomic scale self-formation processes of chemical particles (atoms, molecules and micro crystals). The chemical particle is formed as a result of spontaneous broken of local symmetries of electron quantum field in some compact spatial-temporary carrier in physical space. Topological boundary conditions provide that the compact chemical particle is governed by quantum mechanical postulates and some finite wave function. The particle is revealed as an elementary building block for the next grade of materials design: self-assembling of the supramolecules and nanostructured solids from a set of compact molecules and micro-crystals. Topological electronic exchange junctions of compact chemical particles provide a quantum-statistical 'nanostability' of their cluster. There is an exponential decreasing of exchange-correlation intra-particle force when interatomic bond length increases. In contrast to them the exchange-correlation inter-particle force in supramolecular cluster or in nanostructured solids vanishes very quickly when bond length exceeds some critical value. It is a typical contact force. There is a next material design scale level of thermo statistical systems of nanoparticles. Nonexchange long-distant forces govern these processes. These forces are polynomial decreasing when interatomic bond length increases to the infinity.

- A/PI.26** METRIC-TENSOR FLEXIBLE-CELL ALGORITHM FOR ISOTHERMAL-ISOBARIC MOLECULAR DYNAMICS SIMULATIONS
E. Hernandez, Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus de Bellaterra, 08193 Barcelona, Spain
An extended Hamiltonian approach to conduct isothermal-isobaric molecular dynamics simulations with full cell flexibility is presented. The components of the metric tensor are used as the fictitious degrees of freedom for the cell, thus avoiding the problem of spurious cell rotations and artificial symmetry breaking effects present in the original Parrinello-Rahman scheme. This is complemented by the Nose-Poincare approach for isothermal sampling. The combination of these two approaches leads to equations of motion that are Hamiltonian in structure, and which can therefore be solved numerically using recently developed powerful symplectic integrators. One such integrator, the generalised leap-frog, is employed to provide a numerical algorithm for integrating the isothermal-isobaric equations of motion obtained.
- A/PI.27** REGULAR CHAINS OF NANOCRYSTALS FABRICATED FROM NANOWIRES - PREDICTIONS BASED ON KINETIC MC SIMULATIONS
T. Mueller, K.-H. Heinig, W. Moeller, Research Center Rossendorf, Institute of Ion Beam Physics and Materials Research, PO Box 51 01 19, 01314 Dresden, Germany
The fabrication of regularly arranged nanostructures remains a challenge of today's materials research. In this contribution, Kinetic 3D Lattice Monte Carlo (MC) simulations of the shape evolution of single crystalline nanowires by thermally activated interface diffusion will be presented. Interface minimizations leads to the Rayleigh (or pearling) instability; during annealing nanowires develop peristaltic thickness undulations, which finally results in the decay of the wire into a regular chain of nanocrystals (NC's). For temperatures above the roughening transition it could be shown that size and spacing of the NC's are in good agreement with results of the classical stability analysis performed by Rayleigh and Mullins. The competition between peristaltic undulations having different wavelength (modes) results in the decay of the wire into equal-spaced NC's due to self-selection of the fastest growing mode. This mode selection is demonstrated by the Fourier analysis of the MC results. Other than in the analytical stability analysis it has been found that short-wavelength modes develop first, whereas long-wavelength modes are missing initially. Below the roughening transition, the results differ quantitatively. The spacing between NC's becomes larger and depend on the crystal orientation of the nanowire, which is due to the anisotropy of the interface energy.
- A/PI.28** ATOMIC SCALE COMPUTER AIDED DESIGN FOR NOVEL SEMICONDUCTOR DEVICE
A. La Magna(a), P. Alippi(a), L. Colombo(b), Matthias Strobel(a), (a)CNR-IMM Stradale Primosole 50, 95121 Catania, Italy, (b)INFN and Dipartimento di Fisica, Università di Cagliari, Cittadella Universitaria, 09042 Monserrato (Ca), Italy
Conventional simulation tool for microelectronic technological processes are based on a single framework, i.e. the numerical resolution of continuum evolution equations. Such framework will be soon obsolete since the scaling-down of semiconductor devices requires atomic scale design. In this context it is unlikely that a single approach could guarantee both an accurate and efficient modeling for the different processes. Indeed only the concurrent use of different complementary methodologies can satisfy such demands. We have singled out a series of approaches which can be fruitfully applied, ranging from the force-field based simulation to the kinetic Monte Carlo. The choice of appropriate methodology depends on the peculiar problem we must address. We demonstrate that approaches based on atomic particle-particle potential (e.g. lattice kinetic Monte Carlo or semi-empirical Molecular Dynamics) should be applied when the kinetic evolution occurring during the processes is characterized by rearrangement in different structural identities (e.g. film growth or dopant diffusion near and over the solubility threshold). In turn approaches based on the complex energetic (e.g. kinetic Monte Carlo) are appropriate if material modification is not influenced by the micro-structural evolution (e.g. aggregate ripening). We will report some application examples to doping, deposition and etching manufacturing processes for Si-based devices.
- A/PI.29** BULK ELASTIC PROPERTIES OF COMPLEX CRYSTALLINE MATERIALS
Eleni Ziambaras and Elsebeth Schröder, Dept. Applied Physics, Chalmers University of Technology and Göteborg University, 41296 Gothenburg, Sweden
For materials with a complex crystal structure the characterization and prediction of bulk properties is important. We present a method for evaluating the equilibrium lattice constants and the elastic properties from total-energy calculations for such materials described by multiple lattice parameters and/or a non-trivial atomic basis. A multidimensional polynomial fit of the total energy as a function of all relevant external and internal structural parameters is the basis for a direct and analytical determination of the elastic properties, such as the bulk modulus and bulk-modulus pressure derivative. In contrast to other theory approaches there is no need of the intermediate step of explicitly determining the hydrostatic path. We illustrate the method by calculating total energy data by first-principles density functional theory for a number of materials with different structural properties, e.g. for the wurtzite (2H polytype) and zinc-blende (3C polytype) phases of SiC.

- A/PI.30** ATOMISTIC SIMULATIONS OF SURFACE COVERAGE EFFECTS IN ANISOTROPIC WET CHEMICAL ETCHING OF CRYSTALLINE SILICON
M.A. Gosalvez, A.S. Foster, R.M. Nieminen, Laboratory of Physics, Helsinki University of Technology, 02015 Espoo, Finland
Atomistic simulations of anisotropic wet chemical etching of crystalline silicon using a continuous Cellular Automaton have been performed in order to clarify the dependence of the etch rate of any crystallographic orientation on the amount of OH-coverage and OH-clustering. It is shown that the etch rate is a non-monotonic function of the amount of OH-coverage and that there always exists a value of the OH-coverage at which the etch rate reaches a maximum value. As a result, the dependence of the fastest-etched plane orientation on coverage is obtained implicitly and predictions of convex-corner underetching structures are made.
In addition, we show that the etch rates are described by a linear law in the low coverage region if clustering of OH groups occurs at the surface. However, for conditions preventing clustering, the etch rates are described by a power law where the exponent is greater than 1.
Finally, by interpreting the geometrical restrictions imposed by the interactions between the terminating species, the anisotropy of the etching process is shown to be a trade-off between etch pitting and step propagation at both (111) and (100) (and other high-index) surfaces.
- A/PI.31** MONTE CARLO SIMULATIONS OF THE FRACTAL GROWTH OF THIN FILMS UNDER BALLISTIC OR DIFFUSIVE DEPOSITION
R. Miranda, A.M. Cadilhe and M.D. Ramos, Centro de Fisica do Departamento de Fisica da Universidade do Minho, 4710-057 Braga, Portugal
We performed a comparative study of the growth under two different experimentally relevant conditions, namely, ballistic and diffusive deposition using a Monte Carlo simulation of a suitable lattice-gas model. We characterized the resultant films for their density, roughness, and void size distribution. On the basis of such results we were able to develop a semi-quantitative phenomenological model to explain the bulkiness of such fractal structures. Our results may prove useful to the analysis of experimental data of which mechanism is predominant during growth and in the evaluation of the underlying film microstructure.
- A/PI.32** MONTE CARLO MODELING OF AMORPHIZATION RESULTING FROM ION IMPLANTATION IN Si
Lourdes Pelaz, Luis A. Marques, Maria Aboy, George Gilmer*, Luis A. Bailon, Juan Barbolla, Departamento de Electronica, Universidad de Valladolid, Campus Miguel Delibes, 47011 Valladolid, Spain, *Agere Systems, 600 Mountain Avenue, Murray Hill NJ 07974, USA
The scaling of Si devices to smaller sizes imposes requirements for high dose and low energy implants that may result in the formation of an amorphous layer. We have extended the Kinetic Monte Carlo simulator DADOS to account for the generation of amorphous regions during implantation. We use a binary collision code to generate the implantation cascades. Molecular Dynamics simulations provide the basic parameters and mechanisms to describe defect interactions. In the model, the lattice distortion generated by an interstitial and a vacancy before its annihilation ("the bond defect") plays an important role in the description of the damage resulting from ion implantation in Si. A single set of parameters allows the description of defect evolution from isolated point defects and defect clusters to the formation of continuous amorphous layers. The dynamic anneal that may occur as the implant proceeds establishes a critical temperature above which amorphization is prevented. The model also takes into account the presence of the excess atoms that may have been implanted within an amorphous layer. In this case, most of the excess interstitials generated by the implantation are swept to the surface as the amorphous layer regrows, and do not diffuse in the crystalline region. This process reduces the amount of transient enhanced diffusion during annealing compared to non amorphizing implants of the same dose.
- A/PI.33** THE ROLE OF THE BOND DEFECT ON SILICON AMORPHIZATION: A MOLECULAR DYNAMICS STUDY
L.A. Marqués, L. Pelaz, M. Aboy, J. Vicente and J. Barbolla, Departamento de Electronica, Universidad de Valladolid, E.T.S.I. de Telecomunicacion, 47011 Valladolid, Spain
The modelling of the ion-beam induced amorphization of silicon is important for process simulation because of the use of increasingly high ion implantation doses in the microelectronics industry. We have developed an atomistic model for the silicon amorphization based on the so-called "bond defect", which consists of a local distortion of the silicon lattice with no excess or deficit of atoms. It can be formed by a pure collisional process or by incomplete interstitial-vacancy recombination. We have determined the configuration, energetics and stability of the bond defect using molecular dynamics simulation techniques. We have obtained that the defect lifetime at room temperature is of a few microseconds, very short to justify damage accumulation at usual implantation parameters. However, we have observed that the interaction between close bond defects can create more stable structures which behave as the amorphous pockets created by ion irradiation. We have seen as well that the recombination of a given amount of damage created by bond defect accumulation depends of its spatial distribution: when bond defects are scattered they recombine much faster than when concentrated. This fact allows to define an atomistic model of amorphization based on bond defect recombination depending of the number of neighboring bond defects. The model has been successfully used to reproduce ion-beam amorphization experiments at several doses, dose rates and temperatures.

A/PI.34

TRANSDUCER AND SUPERCONDUCTOR ON BASE OF BORON-BASED NANOTUBES AND 2D CRYSTALS

V.V. Pokropivny, Institute for Problems of Materials Science of UNAS, 03680 Kiev-142, Ukraine

Nanotubes (NTs) are commonly accepted to have unique electronic, mechanic, optic and other properties. The reason is a phase transition connected with change symmetry 3D \rightarrow 1D under reducing of tube diameter up to nanolevel - a nanotube become a quasi-1D quantum unit, but macroscopic in length. Furthermore a packed 2D lattices and ordered bundles or ropes of NTs is expected to be a more unique crystals of top importance as being both a quantum and macroscopic crystals with extended inner porous surface.

2D Lattice of superconducting noncarbon NTs was at first suggested as an ideal superconductor with record critical temperature T_c [1,2]. Mechanism of superconductivity was proposed on base of a whispering mode of phonon vibration which is shown to be responsible for a strong enhancement of electron-phonon interaction and for an increase of T_c and J_c . Coherent and low attenuated vibrations of all atoms pairs on diameter-opposite walls of NTs induce the coherent states of their nearest electrons pairs with opposite impulses $(-k, k)$ that provide an ideal conditions for Cooper pairing and Bose-Einstein condensation.

Superconducting properties of NTs are reviewed, especially a recent discovery of new hexagonal MgB_2 superconductor with $T_c=39$ K by Finnemore et al., and some indications of a possible room- T_c super-conductivity with $T_c=400$ K in carbon NTs bundles by Zhao & Wang. Four routes were proposed to synthesize such the MgB_2 record nanotubular superconductors.

Vibrative properties of NTs are reviewed, especially their peculiar whispering gallery modes, such a high frequency breathing A_{1g} , silent E_{1u} and squash E_{2g} modes. In addition to their low attenuation, the BN-nanotubes posses a charge transfer and the piezoelectric properties as a result. Hence this NTs may serve as powerful electroacoustic transducers in giga- and tera-hertz range. Accounting the propagation of an ultrasound is possible in crystals only, we can suggest a hypersound generator and detector on base of BN nanotube with SiC core, that was synthesized recently.

2D nanotubular crystals promise to be the best photonic crystals, collar cells, effective gas membranes, etc., that allow us to call them as miracle-crystals.

[1]V.V. Pokropivny. Room- T_c superconductivity on whispering mode in quasi-1D composite of superconducting nanotubes. Is it possible?// J.Superconductivity 13,607 (2000)

[2]V.V. Pokropivny. Composite on base of 2D nanotubular lattice as ideal high- T_c superconductor // Physica C 351, 71 (2001).

Thursday, June 20, 2002
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Session V: Catalysis

- 09:00 **A-V.1** **CATALYTIC CONVERSION OF HYDROCARBONS IN ZEOLITES FROM FIRST PRINCIPLES**
Lubomir Benco(a), Thomas Demuth(a), Francois Hutschka(b), (a)Institut fuer Materialphysik and Center for Computational Materials Science, Universitaet Wien, Austria, (b)Totalfinaelf, Centre Europeen de Recherche et Technique, Harfleur, France
Conversion of hydrocarbons over zeolites is important industrial process used in the production of petrol. The microscopic steps of the conversion, however, are still not fully understood. In order to examine reaction pathways we have performed static and molecular dynamics DFT calculations on gmelinite zeolite and linear saturated and unsaturated hydrocarbon molecules. The conversion can proceed through the through the chemisorption of olefins at the inner surface of the zeolite. The desorption of chemisorbed species produces unstable protonated molecules. The protonated hydrocarbons are long-lived being stabilized in the zeolite surroundings. They are considerably deformed and at increased temperatures (~700K) high mobility of the H atoms along the molecular chain is observed. The relocation of the H atom can lead to the formation of structures with maximum stabilization of the positive charge, such as molecules with tertiary C atoms and cyclo-structures of hydrocarbons. The back donation of the proton to the zeolite framework can cause collapse of the linear protonated molecule, as well. Both cracked and isomerized products can be formed upon the back donation. Depending on the O...H-C contact established between the molecule and the framework the H atoms are removed from different C atoms thus starting either cracking or isomerization of the hydrocarbon molecule.
- 09:40 **A-V.2** **DYNAMICS OF HYDROGEN MOLECULES ON METAL ALLOY SUFACES-PROBING LOCAL SURFACE REACTIVITY WITH HYDROGEN**
Wilson Agerico Dino(a), Katsuyuki Fukutani(a), Tatsuo Okano(a), Hideaki Kasai(b), Ayao Okiji(c), Daniel Farias(d) and Karl-Heinz Rieder(e), (a)Institute of Industrial Science, The University of Tokyo, Meguro-ku, Tokyo 153-8505, Japan, (b)Department of Applied Physics, Osaka University, Suita, Osaka 565-0871, Japan, (c)Wakayama National College of Technology, Gobo, Wakayama 644-0023, Japan, (d)Departamento de Fisica de la Materia Condensada C-III, Universidad Autonoma de Madrid, Cantoblanco, 28049 Madrid, Spain, (e)Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany
The hydrogen on metal surfaces system has, through the past years, become a paradigm for studying dynamical quantum processes on solid surfaces. Previously, we presented reports on the dynamics of H₂ on single component metal surfaces, focusing on the orientational dependence of hydrogen-metal surface reactions. We then extended our study to consider the dissociative adsorption dynamics of H₂ interacting with a metal alloy (esp., binary component) surface, viz., Cu₃Pt(111). Here, we compare the dynamics of H₂ reaction with two binary component metal surfaces, viz., Cu₃Pt(111) and NiAl(110). We will show how scattering dynamics studies, complementing dissociative adsorption studies, could give us a microscopic picture of why H₂ dissociation on Cu₃Pt(111) is globally non-activated, and activated on NiAl(111). We will discuss the dynamics of H₂-solid surface interaction in the context of the feasibility of utilizing H₂ as a unique experimental tool to directly probe the adsorbate-surface interaction potential, etc. (KEYWORDS: hydrogen, deuterium, metal alloy, scattering dynamics, potential energy surface, dynamics calculation, ab initio quantum dynamics calculations, Cu(111), Pd(111), Cu₃Pt(111), NiAl(110))
- 10:00 **A-V.3** **COMPUTER SIMULATION OF SPUTTERING AND OXYGEN DESORPTION PROCESSES AT GRAZING ION BOMBARDMENT OF Ag(110) SURFACE**
A.A. Dzhurakhalov, S.E. Rahmatov, N.A. Teshabaeva, Arifov Institute of Electronics, F.Khodjaev Str.33, 700187 Tashkent, Uzbekistan
The sputtering and desorption processes give the information about crystal structure and property of materials and vacuum devices.
In the present work the ion sputtering and oxygen desorption processes at 5 keV Ne ion bombardment of clean and oxygen covered Ag(110) surface have been investigated by computer simulation. The trajectories of the colliding particles were constructed as a sequence of binary collisions. The particle interactions were described by the universal Biersack-Ziegler-Littmark potential. The inelastic energy losses have been calculated by modified Firsov model and included into the scattering kinematics. The presence of a planar energy barrier on the surface was taken into account.
The energy and angular distributions of particles sputtered and desorbed from the surface, as well as their yields have been calculated as a function of polar and azimuth angle of incidence. The dissociative and non-dissociative desorption yields of oxygen admolecules have been studied in detail. In the angular distributions of desorbed particles the maxima corresponding to the preferential ejection directions have been observed. It was established that in the case of grazing ion bombardment the probability of non-dissociative desorption of diatomic molecules is large and depends strongly on crystal orientation.
Application of calculated results to study the sputtering and desorption processes on the single crystal surface under grazing ion bombardment is discussed.
- 10:20 **BREAK**

Symposium A

- 10:40 **A-V.4** **WHY IS A NOBLE METAL CATALYTICALLY ACTIVE? THE ROLE OF THE O-AG INTERACTION IN THE FUNCTION OF SILVER AS AN OXIDATION CATALYST**
Catherine Stampfl, Weixue Li, Matthias Scheffler, Fritz-Haber-Institut der Max Planck Gesellschaft, Berlin-Dahlem, Germany
Silver is an important industrial catalyst for the epoxidation of ethylene to epoxide and the partial oxidation of methanol to formaldehyde; two of the most versatile chemical intermediates. Despite huge research efforts [1,2], due to the pressure and materials gap separating the real world of catalysis from the ideal world of well-characterized standard Surface Science experiments, there is an acute lack of understanding of the function of silver as an oxidation catalyst on the microscopic level. Extensive density-functional theory calculations, and taking into account temperature and pressure, provide a comprehensive picture of the behavior and interaction of oxygen and silver, and help explain why silver, as a noble metal which binds adparticles only weakly, is a remarkably efficient catalyst. Among other things we find that low coverages of oxygen chemisorbs on Ag(111), but for coverages greater than ~ 0.25 -ML sub-surface sites are occupied and surface-oxide like structures form. Sub-surface oxygen as well as defects significantly strengthen the surface oxygen-metal bond, allowing oxygen to stay on the surface and to participate in reactions. At the very high temperatures (~ 900 -K) of certain oxidizing reactions, however, only oxygen species adsorbed at pre-existing surface defects are thermodynamically stable.
[1] R. A. van Santen and H. P. C. E. Kuipers, Adv. Catal. 35, 265 (1987).
[2] A. Nagy et al. J. Catal. 188, 58 (1999).
- 11:20 **A-V.5** **THE $\sqrt{3} \times \sqrt{3}$ RECONSTRUCTION OF ALUMINA(0001)**
Thierry Deutsch, CEA-Grenoble DRFMC/SP2M Frédéric Lançon, CEA-Grenoble DRFMC/SP2M, France, Igor Vilfan, Inst. J. Stefan, Ljubljana, Slovenia
We present a new method of obtaining the real-space structure of complex surface reconstructions from incomplete scattering data. Usually, the experiments provide us only the non-integer-order diffraction intensities and, after Fourier transform, an incomplete Patterson map. Computer simulations based on the energy minimisation are implemented to obtain the missing intensities of the integer-order peaks and the structural information from such a map. The method is used to analyse the atomic structure of the Al-rich $\sqrt{3} \times \sqrt{3}$ reconstructed surface of sapphire α -Al₂O₃(0001). In the simulations, the interactions between the Al overlayer atoms were described with the Sutton-Chen potential and the interactions between the overlayer and the sapphire substrate with a laterally modulated Lennard-Jones potential. We have shown that the hexagonal reconstructed unit cell is composed of triangles where the two layers of Al adatoms are FCC(111) ordered whereas between the triangles the stacking is FCC(001).
- 11:40 **A-V.6** **ATOMISTIC VIEW OF THE HETEROEPITAXY ON AN INHOMOGENEOUS SUBSTRATE**
Christine Goyhenex, Hervé Bulou, Carlo Massobrio, CNRS, IPCMS, 23 rue du Loess, 67037 Strasbourg Cedex, France
The ability to incorporate nanostructures in fields like microelectronics or magnetic recording is a challenge for the developments towards high density storage and large-scale integration. The main difficulty is to produce large quantities of nanostructures in a controlled manner. The herringbone surface reconstruction of Au(111) offers an efficient way to grow collections of clusters homogeneous both in size and density.
Many experiments have been carried out on systems where X species (X=Fe,Co,Ni,Cu,Rh) nucleate at the kinks sites of the Au(111) reconstruction leading to regular arrays of clusters. However the understanding at the atomic scale of the organization of these systems is far from being complete. This is mostly due to the complex morphology of the substrate giving rise to a wide distribution of bond distances when atoms are deposited on it. In this contribution, we present a study of the system Co/Au(111) in the framework of atomistic tight-binding molecular dynamics simulations.
The inhomogeneous strain state of the gold reconstructed surface is expected to play an important role in the microscopic mechanisms of the growth. Therefore we focus on the local hydrostatic stress maps to characterize the stress distribution and its modifications upon adsorption and incorporation of Co atoms in the surface. First results on the effect of the inhomogeneity of the substrate on atomic diffusion will be also shown.

12:00

LUNCH

Thursday, June 20, 2002
Jeudi 20 juin 2002Afternoon
Après-Midi

Session VI: Bio Molecules & Polymers

- 14:00 **A-VI.1** **FREE ENERGY SIMULATIONS COME OF AGE: PROTEIN--LIGAND RECOGNITION**
Thomas Simonson, CNRS, Strasbourg, France, Georgios Archontis, U.of Cyprus, and Martin Karplus, U. of Strasbourg & Harvard University, USA
In recent years, molecular dynamics simulations of biomolecular free energy differences have benefited from significant methodological advances and increased computer power. Applications to molecular recognition provide an understanding of the interactions involved that goes beyond, and is an important complement to, experimental studies. Poisson-Boltzmann electrostatic models provide a faster and simpler free energy method in cases where electrostatic interactions are important. We illustrate both molecular dynamics and Poisson-Boltzmann methods with a detailed study of aminoacid recognition by aspartyl-tRNA synthetase, whose specificity is important for maintaining the integrity of the genetic code.
T. Simonson, G. Archontis, M. Karplus (2002) *Accts Chem. Res.*, in press; G. Archontis, T. Simonson (2001) *J. Am. Chem. Soc.*, in press (online version at http://pubs.acs.org/subscribe/journals/jacsat/browse_asap.html); G. Archontis, T. Simonson, M. Karplus (2001) *J. Molec. Biol.* 306:307-27. T. Simonson (2001) *Current Opinion in Structural Biology*, 11:243-52.
- 14:40 **A-VI.2** **AB INITIO TIGHT-BINDING STUDY OF EXCITON OPTICAL AND ELECTRO-OPTIC PROPERTIES OF CONJUGATED POLYMERS**
Thomas G. Pedersen and Thomas B. Lyngé, Institute of Physics, Aalborg University, Pontoppidanstraede 103, 9220 Aalborg East, Denmark
Recovery of implantation defects is of paramount importance for applications of SiC in semiconductor devices. Up on implantation heavy ions produce along their tracks amorphous zones, which when overlapping at high fluences ($>10^{14}$ cm⁻²) form a continuous amorphous band. Crystallization of this band requires temperatures higher than 8000C, while crystallized material might consist of many polytypes of SiC with different properties, hampering economic production. It is known that crystalline SiC can be prevented from turning amorphous by choosing implantation temperatures above 6000C. Therefore, it is likely that single cascade damage will recover at about this temperature. In order to perform a detailed study on the recovery of amorphous zones created by individual ions, defects created by very low fluences of Xe ions have been monitored by PBA. Positrons are very sensitive to defects, so that at fluences as low as $4 \cdot 10^8$ 420 keV Xe cm⁻² positron trapping has been observed. The fraction of positrons trapped in defects corresponds to results of a model where diffusion limited trapping was assumed in disordered zones predicted on the basis of SRIM calculations. The fraction increased linearly with fluence and saturation effects appeared at fluences $>5 \cdot 10^{12}$ cm⁻². Similar implantations in Si and diamond, which are no compound materials, induced much less damage. Thermal recovery and recovery kinetics of the amorphized zones in 6H-SiC and in epitaxial 3C-SiC on Si are discussed.
- 15:00 **A-VI.3** **PPV AND PDA INTRA-MOLECULAR CHARGE MOBILITY SIMULATED BY QUANTUM MOLECULAR DYNAMICS**
A.M. Almeida, Marta M.D. Ramos and Helena G. Correia, Departamento de Fisica, Universidade do Minho, Largo do Paço, 4700-320 Braga, Portugal
The growing interest in organic semiconductor based devices together with the most recent computational facilities has allowed the extensive use of simulations to study large molecular systems anticipating some of their individual physical properties.
The simulation of a device such as a light emitting diode (LED), whose active media is a polymeric material, demands a well-founded knowledge of how a molecule behaves under specific conditions, namely how an injected charge accommodates in a molecule and the way it drifts under the action of an external electric field.
The results presented here refer to two wide used polymers (poly(p-phenylene-vinylene) (PPV) and poly-diacetylene (PDA)) showing how small and medium size molecules, either with a single net charge or containing an exciton, respond to an external electric field.
In our calculations we have used a self-consistent quantum molecular dynamics method, which has the ability for simulating the transport of the injected charge along each molecule, thus providing an estimate of the charge mobility. Our results suggest there are two charge conduction regimes. The minimum value of the electric field strength to cause charge displacement was also predicted. Differences have been found in the charge mobility depending on the polymer chemistry. The effect of stretching of the PPV molecule has also been studied.

15:20 **A-VI.4** **APPLYING PERIODIC DENSITY FUNCTIONAL THEORY METHODS FOR SOLID STATE CHEMICAL PHYSICS ? MODELLING INTER AND INTRA-MOLECULAR INTERACTIONS IN BIOLOGICALLY RELEVANT HYDROGEN-BONDED NETWORKS**

Mark Johnson, Institut Laue Langevin, Grenoble, France

The extension of quantum chemistry methods from small isolated molecules to periodic solids containing up to ~1000 atoms has allowed the focus of computational work in chemical physics to shift from intra- to inter-molecular interactions. The quantum tunnelling of molecular rotors is a simple, extremely sensitive probe of inter-molecular interactions and has been used to evaluate solid state density functional theory (DFT) methods in this context. Molecular vibrations constitute an intrinsically more complex, multi-dimensional problem, but the same DFT methods generally allow vibrational spectral profiles, measured by inelastic neutron scattering, to be accurately reproduced. In particular solid state methods are particularly well suited to modelling vibrational modes in hydrogen-bonded systems in which the inclusion of such strong inter-molecular interactions can shift the single molecule frequencies by a factor of two. Calculations on model hydrogen-bond compounds will be shown; hydrogen-bonded dimers, one-dimensional hydrogen-bonded molecular chains, bases and nucleosides in higher dimensional hydrogen-bonded networks. Perspectives for moving, experimentally and computationally, on to ?real? hydrogen-bonded systems, like DNA and polypeptides, will be discussed.

15:40

BREAK

16:00-18:00

POSTER SESSION II

A/PII.01

FRACTAL DIMENSION OF ZEOLITE CATALYSTS

Francisco Torrens, Institut Universitari de Ciència Molecular, Universitat de València, Dr. Moliner 50, 46100 Burjassot (Valencia), Spain

Atom-atom analyses of the geometric descriptors, topological indices and fractal dimension D are applied to active-site models of Brønsted acid zeolites. The results are compared with those from the literature for rings and cavities. A method is tested similar to that used in previous works for crystal fragments. The obtained results are encouraging and the good quality of the attained analysis is clear from the comparison with cavity results. The active sites are modelled by sets of Al-OH-Si units. These bridges form 2?12-membered rings. Indices for the models are calculated. The analysis shows that the maximal $D(\text{Si})$ contribution corresponds to the 6-ring, matching to the maximal $D(\text{cavity})$. It is suggested that Si plays a main role in the catalytic activity. Most cavities show no fractal character, while for the 6?8-cavities D is the greatest and is maximal for the 6-cavity, which is expected to be the most reactive. This is in agreement with the greatest flexibility and with the adsorption of ions in the 6-ring reported in the literature. Work is in progress to test the effect of local deformations on the opening and closing of ring apertures and to check the role of Si.

A/PII.02

CALCULATIONS OF THE ELECTRONIC AND ATOMIC STRUCTURE OF POINT DEFECTS, POLARONS AND EXCITONS IN ABO₃ PEROVSKITE CRYSTALS

R.I. Eglitis, University of Osnabrueck, Fachbereich Physik, 49069 Osnabrueck, Germany, E.A. Kotomin, Max Planck Institut für Festkörperforschung, 70569 Stuttgart, Germany, G. Borstel and S.E. Kapphan, University of Osnabrueck, Fachbereich Physik, 49069 Osnabrueck, Germany, V.S. Vikhnin, A.F. Ioffe Physico-Technical Institute, Saint-Petersburg, Russia and N.E. Christensen, Institute of Physics and Astronomy, Aarhus University, Aarhus-C 8000, Denmark

We review our recent achievements in computer simulations of point defects in advanced perovskite crystals[1]. Quantum chemical INDO calculations confirm the existence of the self-trapped electrons in KNbO₃, KTaO₃ and BaTiO₃ crystals associated with the lattice relaxation energy of 0.21 eV, 0.27 eV and 0.24 eV as well as estimated optical absorption of 0.78 eV, 0.75 eV and 0.69 eV, respectively. An electron in the ground state occupies t_{2g} orbital of Nb⁴⁺, Ta⁴⁺ or Ti³⁺ ion. The relevant experimental data are discussed[2].

It is shown, by means of INDO calculations, that polaronic-type charge transfer vibronic excitons (CTVEs) in ferroelectric oxides could lead to the formation of a new phase – the phase of charge transfer vibronic excitons[3].

We suggest a theoretical interpretation of the green luminescence in ABO₃ perovskite crystals as a result of the recombination of electrons and holes forming a CTVE. Our calculated luminescence energies for SrTiO₃, BaTiO₃, KNbO₃ and KTaO₃ perovskite crystals - 2.34 eV, 2.30 eV, 2.17 eV and 2.14 eV are in good agreement with the experimentally observed luminescence energies.

[1] J.T. Devreese, V.M. Fomin, E.P. Pokatilov, E.A. Kotomin, R.I. Eglitis, Yu. Zhukovskii, Phys. Rev. B 63, 184304 (2001).

[2] R.I. Eglitis, E.A. Kotomin, G. Borstel, Comp. Mat. Sci. 21, 530 (2001).

[3] V.S. Vikhnin, R.I. Eglitis, S.E. Kapphan, E.A. Kotomin, G. Borstel, Europhys. Lett. 56, 702 (2001).

- A/PIL.03** FORMATION OF OLIGOMERS IN COURSE OF TiCl₄ AMMONOLYSIS AND THEIR ROLE IN Ti(IV)-Ti(III) REDUCTION PROCESSES: A THEORETICAL STUDY
A.Y. Timoshkin, M. Siod-miak, G. Frenking Fachbereich Chemie, Philipps-Universität Marburg, 35032 Marburg, Germany, A. A. Korkin, Advanced Systems Technology Lab, Motorola Inc., Mesa AZ 85202, USA
Formation of oligomer species in the gas phase during CVD is favorable for the group 13 nitrides[1]. Thermodynamics aspects of formation of oligomers during TiCl₄ ammonolysis are considered in the present report. In previous theoretical studies (2,3) it was found, that Cl₃TiNH₂ is a dominant product in the gas phase at 600-1400 K. For the [Cl₃TiNH₂]₂ and [Cl₂TiNH], several possible isomers (with NH₂, Cl, NH, H bridging groups) have been considered. All structures were fully optimised at HF and B3LYP level of theory with DZP quality basis set (ECP on Ti and Cl) and correspond to minima on PES. Dimerization processes were found to be exothermic by about 10 kcal/mol, but strongly disfavoured by the entropy. Tetrameric cluster [ClTiN]₄ is predicted to be viable only at T>1500 K. Study of the Ti(IV) to Ti(III) reduction involving dimeric species reveals that additional coordination of ammonia to the [Cl₃TiNH₂]₂ facilitates elimination of Cl atom.
[1] Timoshkin A.Y., Bettinger, H.F., Schaefer H.F. J. Cryst. Growth, 2001, 222, 170. 2. Siodmiak, M.; Frenking, G.; Korkin, A. J. Mol. Model. 2000, 6, 413. 3. Umanskii, S.Ya., Novoselov, K.P.; Minushev, A.Kh.; Siodmiak, M.; Frenking, G.; Korkin, A. J. Comp. Chem., 2001, 22, 1366.
- A/PIL.04** EMBEDDED-ATOM SIMULATION OF TITANIUM-GROWTH INCLUDING GRAIN-BOUNDARIES
Thomas Hammerschmidt and Peter Vogl, Walter Schottky Institut, Technische Universität München, 85748 Garching, Germany
Titanium is a well-known barrier-layer-film for aluminium metallization. During ionized physical vapor deposition, it forms grains of predominantly (0001) orientation and of several nanometers size which is of the order of or smaller than the typical diffusion length for relevant growth temperatures. A quantitative understanding of epitaxial growth of titanium therefore calls for atomistic molecular dynamics and Monte Carlo simulations that take into account the diffusion across grain boundaries. We have performed such studies with an accurately modeled embedded atom potential for titanium that is based on published potentials but has been refined such that surface diffusion barriers, atomic cluster properties, and surface relaxations are accurately captured. Since many grain-boundaries can be derived from coincidence-site-lattices which accommodate both ideal unit cells as well as tilted ones, we have specifically modeled hcp-tilt-grain boundaries perpendicular to the (0001) axis. After energetically relaxing these grain boundaries, we have calculated the energy-barriers for inter-grain-diffusion and intra-grain-diffusion on different facets. In a molecular dynamics simulation, we have investigated the growth of a few mono-layers in the presence of grains of various orientations.
- A/PIL.05** ORDERING KINETICS IN Ni₃Al BY MOLECULAR DYNAMICS
P. Oramus, M. Kozcowski, R. Kozubski, Institute of Physics, Jagellonian University, Reymonta 4, 30-059 Krakow, Poland, C. Massobrio, V. Pierron-Bohnes, M.C. Cadeville, Institut de Physique et Chimie des Matériaux de Strasbourg, 23, rue du Loess, 67037 Strasbourg, France, W. Pfeiler, Institut für Materialphysik, University of Vienna, Strudlhofgasse 4, 1090 Vienna, Austria
Molecular Dynamics simulations of ordering kinetics in Ni₃Al referred to the previous Monte Carlo (MC) study[1]. The system Hamiltonian was approximated by "embedded-atom" potentials (EAM). The sample of Ni₃Al containing 1372 atoms was initially perfectly L1₂- long-range ordered. After having artificially created 1 vacancy by removing at random 1 Ni-atom, the dynamics of the sample was simulated at constant temperature and pressure. Different types of atomic jumps were observed, whose numbers obeyed the Arrhenius law yielding effective activation energies.
The obtained results lead to the following conclusions:
1. The atoms predominantly migrate by jumps to nn vacancies.
2. The number of antisites systematically increases, being, however, low in comparison to the total number of atomic jumps. Most of the jumps are, therefore, ineffective for ordering kinetics causing only temporary change of the chemical order. The jumps creating antisites are most often followed by reverse jumps.
3. The most probable jumps are those of Ni atom within the Ni sublattice.
4. The Al and Ni atom jumps between different sublattices are correlated. This result is in agreement with the predictions based on the models created after the MC simulations.
5. Antisites are created as nn antisite pairs in the sequence of two highly correlated jumps.
[1] P. Oramus, R. Kozubski, V. Pierron-Bohnes, M.C. Cadeville, W. Pfeiler, Phys.Rev.B 63, 174109, (2001).
- A/PIL.06** MOLECULAR DYNAMICS SIMULATIONS OF SELF-BOMBARDMENT OF COMPACT CLUSTERS ON Pt(111)
D. Adamovic, E.P. Munger, V. Chirita, L. Hultman, J.E. Greene, Theory and Modeling, The Department of Physics and Measurement Technology, 581 83 Linköping, Sweden
Studies of low-energy bombardment of two-dimensional (2D) close-packed clusters are of great importance and strongly related to thin film growth. We use embedded-atom method molecular dynamics simulations to monitor the kinetics characterizing the self-bombardment of Pt₃, Pt₇, Pt₁₉ and Pt₃₇ clusters on Pt(111) at 1000K. Atoms incident perpendicular to the surface with energies between 5 and 50 eV are followed in separate simulations of ~ 20 ps each. Clusters are divided into different sections, outer, rim and core area respectively. Our simulations reveal three major classes of events. They are cluster preservation, i.e. no change in shape or position, cluster reconfiguration, involving edge-diffusion and/or concerted dimer/trimer gliding and cluster disruption (rim atom scattering and/or total disintegration). Two of the most commonly observed events are the formation of three-dimensional (3D) clusters and the hopping and/or push out/exchange mechanism with rim atoms. Other typical processes observed are the permanent or temporary dislodgement of cluster atoms onto the surface as well as the creation of surface vacancies. Our results suggest that cluster preservation and reconfiguration events primarily occur with incident atom energies below 30 eV, while cluster disruption and surface vacancy formation events prevail at higher energies.

Symposium A

- A/PIL.07** **MODIFIED SUTTON-CHEN POTENTIALS FOR METALLIC ALLOYS**
H. Aourag, H. Feraoun and C. Coddet, LERMPS, Université de Technologie de Belfort-Montbeliard, Site des Sévenans, 90010 Belfort, France
The analytic construction of a many body potential inspired from the Sutton-Chen parametrization is presented for copper and silver. A new approach is used to model the cross interaction for the Cu-Ag alloys. The parameters are fitted to first principles calculations based on the full potential linear plane wave method (FPLAPW). The structural properties of the order and disorder Cu-Ag alloys in the B2 and FCC structures are presented for different concentrations.
- A/PIL.08** **INFLUENCE OF MANY-BODY INTERACTIONS ON RESISTANCE OF A GRAIN BOUNDARY WITH RESPECT TO A SLIDING SHIFT**
Simon Dorfman, Department of Physics, Technion - Israel Institute of Technology, 32000 Haifa, Israel, David Fuks, Department of Materials Engineering, Ben-Gurion University of the Negev, POB 653, Beer-Sheva, Israel, Luiz A.C. Malbouisson, Institute of Physics, Federal University of Bahia, Salvador, Ba, Brazil, Kleber C. Mundim, Instituto de Quimica, Universidade de Brasilia, Caixa Postal 4478, 70919-970 Brasilia, Brazil, Donald E. Ellis, Department of Physics and Astronomy, Northwestern University, Evanston IL 60208, USA
A three-body potential for W, which is constructed within a recursion procedure from ab initio calculated data, is employed in the study of the sliding of the $\{111\}$ grain boundary of tungsten with the boron impurity. The many-body potential is the potential incorporating directional bonding in contrast with central force many-body potentials such as embedded atom potentials. Forms of interatomic potentials used in our simulations illustrate directly the importance of directional bonding in simulations of sliding for bcc metals. The recursion procedure applied in our simulations gives the possibility to include in regular manner four-body and etc. interactions. We have studied the reconstruction of the $\{111\}$ tungsten grain boundary with a boron impurity and demonstrated the influence of many-body interactions on the resistance of the grain boundary with respect to sliding shift. The distribution of the elastic field in the vicinity of the grain boundary is also considered in our paper.
- A/PIL.09** **OPTICAL AND ELECTRONIC PROPERTIES OF OLIGODIACETYLENES FROM SINGLE CHAIN TO CLUSTERS**
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
In this communication we will present the results of a theoretical investigation carried out using a time dependent Hartree-Fock (TDHF) approach based on the INDO/S Hamiltonian on isolated oligodiacetylenes and on their cluster. We will also report on the effect of the supramolecular architecture on the nature of photogenerated neutral and charged species in these conjugate systems and on the non linear optical properties, which are relevant for their potential applications in photonics.
The theoretical data will be compared with recent experimental results obtained for polydiacetylenes whose different molecular and inter-molecular structure has been obtained through molecular design by attaching particular substituents to the polymer backbone.
- A/PIL.10** **TIGHT-BINDING SECOND-MOMENT INTERATOMIC POTENTIALS FOR AL-BASED ALLOYS DERIVED FROM TOTAL-ENERGY CALCULATIONS**
N.I. Papanicolaou, G.A. Evangelakis, Department of Physics, Solid State Division, University of Ioannina, P.O. Box 1186, 45110 Ioannina, Greece and D.A. Papaconstantopoulos, Center of Computational Materials Science, Naval Research Laboratory, Washington DC 20375-5345, USA
We have obtained interatomic potentials for Al-based binary ordered alloys within the tight-binding model in the second-moment approximation. We have adopted the procedure of fitting to the volume dependence of the total energy of the systems, obtained from first-principles augmented-plane-wave calculations. The resulting potentials have been used to perform molecular-dynamics simulations in order to obtain temperature-dependent quantities, like lattice constants, mean-square displacements, as well as the phonon spectra of the materials. A comparison with existing experimental and theoretical data was made and a satisfactory agreement was found.
- A/PIL.11** **EQUILIBRIUM ENRICHMENT OF THE SURFACE LAYER OF COPPER AND Cu-Al ALLOYS BY VACANCIES**
Yu.Ya. Andreev, A.E. Kuttyrev, E.N. Grishina, MISA, Corrosion of Metals, Leninskiy pr. 4, 117936 Moscow, Russia
According to Ghuchovitsky-Guggenheim equation the surface Gibbs energy for Cu-Al alloys has been calculated for ideal model of solid solution. The concentration of vacancies within surface layer of Cu and Cu-Al alloys $N_v(s)$ at 298 K has been calculated by formula $dG_s = -RT \ln N_v(s)$ according to vacancy thermodynamic model of surface layer. The calculation shows a direct relationship between Al content (at.%) and the value of $N_v(s)$. The value of $N_v(s)$ for pure copper has an order $\lg N_v(s) = -10$ as compared with the bulk $\lg N_v(b) = -20$.
The selective dissolution of Al from Cu-Al alloys has been studied experimentally in 1M NaOH solution. The rate of this process is limited by vacancy mechanism diffusion within surface layer. Using electrochemical method the value of diffusivity D of Al within surface layer was determined for different content of Al. This value increases with increasing contents of Al by straight-line graph and has an order $\lg D = -13$ [cm²/c]. Using the relationship $D = D_v N_v(s)$ the concentration of vacancies within surface layer $N_v(s)$ has been estimated where D_v is a vacancy diffusivity. The values $N_v(s)$ have an order $\lg N_v(s) = -2$. We assume that the high value of D is defined by the threshold value of $N_v(s)$ under a critical electrode potential.

- A/PIL.12** THE RELATIONSHIP BETWEEN THE SURFACE ENERGY OF SINGULAR CRYSTAL FACES AND THE ENERGY OF VACANCY FORMATION FOR CUBIC METALS
Yu.Ya. Andreev, Department of Corrosion of Metals, Moscow State Institute of Steel and Alloy, Leninskiy pr. 4, 117936 Moscow, Russia
Theoretically it was derived that value of reversible surface energy dUs of singular face formation for cubic metals is proportional to the enthalpy of vacancy formation dHv and to coordination number Zad of an adatom as the relationship $dUs = Zad (2dHv/Zo)$ where Zo is the atomic coordination number of cubic metal. For fcc metals with the (111), (100) and (110) singular faces and $Zad= 3, 4$ and 5 , respectively, the value of dUs increase in the order: $dUs(111) > dUs(100) > dUs(110)$ in accordance with experimental data. For bcc metals, the lowest values of dUs calculated for the (110) face ($Zad = 2$) of Nb, Mo, Ta and W are agreement with experimental data on the surface tension for these metals. From the theory follows formula $dGs = -RT \ln Nv(s)$ where dGs is the surface Gibbs energy and $Nv(s)$ is the mole fraction of vacancies within the surface layer of metal. The threshold value of $Nv(s)$ at the near-melting temperature may be as high as 0.01.
- A/PIL.13** AB INITIO MOLECULAR ORBITAL STUDY OF GROUP-III NITRIDE BIRADICALOIDS PRODUCED BY THE METHOD OF PHOTO-DISSOCIATION OF ENERGETIC COMPOUND BEAMS
K. Hayashi, T. Kanayama, T. Shimizu, H. Kojima, Advanced Materials Science R&D Center, Kanazawa Institute of Technology, 3-1 Yatsukaho, Matto, Ishikawa 924-0838, Japan
In order to further develop quantum functional devices it has become indispensable to precisely control the surface reaction pathways of neutral free radicals responsible for the device processing. The problem encountered in the experimental study of a chemical reaction between a neutral free radical and a well-characterized material surface is how to sufficiently supply only the desired free radical species onto the surface. We have proposed several experimental approaches to produce a steady-flux purified beam of neutral free radicals. One of these approaches is the method of photo-dissociation of energetic compound beams (PDECB) where a beam of desired neutral free radical species is efficiently produced from a molecular beam of a purified unimolecular metastable dye by wavelength-selective photolysis using a near-UV CW laser [1-3].
In the present study, search for PDECB source compounds to produce beams of neutral free radicals applicable to low-temperature epitaxial growth of defect-free GaN, AlN, and BN was carried out using molecular design techniques based on post-SCF ab initio molecular orbital methods. We found the corresponding dialkyl group-III azides as unimolecular metastable dyes appropriate for the PDECB sources.
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- A/PIL.14** NONEMPIRICAL STUDY OF THE SITE PREFERENCE OF THE Ti AND Ni ALLOYING IN THE Fe3Al COMPOUND
D. Fuks(a), S. Dorfman(b), V. Liubich(a) and L. Kutsenko(a), (a)Dept. of Materials Engin., Ben Gurion Univ. of the Negev, POB 653, Beer-Sheva, Israel, (b)Dept. of Physics, Technion, 32000 Haifa, Israel
We have done nonempirical calculations of the total energies of ordered DO3 FeAl-phases doped by Ti and Ni in the framework of coherent potential approximation (CPA) within Linear Muffin-Tin Orbitals (LMTO) formalism for different atomic volumes. These calculations allow to obtain mixing potentials for these phases and to use them for the non-empirical determination of the long-range order (LRO) parameters at different temperatures for alloys investigated. The site preference of the Ti and Ni additions was studied.
In our approach the description of the temperature dependencies of LRO and of the free energy of ordering have been carried out according to the concentration wave theory (CW). The CW method allows us to take into account interatomic interactions at arbitrary distances. It establishes the relation between the statistical theory and the Landau-Lifshitz thermodynamical theory of second order transformations in the ordering of alloys. This method provides the possibility of prediction of the structure of the ordered phase if the interatomic interactions are estimated. We combine the SCW theory with the first-principles calculations of the interatomic interaction and evaluate the influence of alloying on the interaction parameters as well as the temperature dependence of the order-disorder phase transformation for ternary alloys.
- A/PIL.15** COUPLING MOLECULAR DYNAMICS AND MONTE-CARLO SIMULATIONS: STUDY OF CoPt ALLOY
M. Allanen, H. Bouzar, Laboratoire de Physique et Chimie Quantique, Faculté des Sciences, Université M. Mammeri, Tizi-Ouzou, Algérie, C. Goyhenex, V. Pierron-Bohnes, CNRS, IPCMS, 23 rue du Loess, 67037 Strasbourg Cedex, France
Monte-Carlo simulations have been established as a useful tool for studying order-disorder phenomena in alloys with a model based on a vacancy-atom exchange and interactions up to the second nearest neighbours, using a Glauber algorithm [2]. However up to now the saddle point energies had been assumed to be all equal in the alloys. We present in this work a more realistic model where the different saddle point energies for vacancy migration are calculated within a Molecular Dynamics approach taking relaxation effects into account. The atomic potentials were determined using a Tight-Binding formalism within the second-moment approximation [3].
We will show that such semi-empirical potentials allow to reproduce reasonably the structure and formation energies of the Co x Pt 1-x alloys. The relaxation effects will be pointed out by comparing the calculation of the four kind of saddle point energies for the vacancy migration before and after applying the relaxation procedure. Finally, first results of Monte-Carlo simulations performed with these new energies will be presented.
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- A/PIL.16** THEORETICAL AND EXPERIMENTAL INVESTIGATION OF ATOMIC LAYER DEPOSITION OF COPPER(I) OXIDE
Tobias Törndahl, Mikael Ottosson, Karin Larsson, Jan-Otto Carlsson, The Ångström Laboratory, Dept. of Materials Chemistry, Box 538, 75121 Uppsala, Sweden
Atomic Layer Deposition (ALD) of copper(I) oxide from copper(I) chloride and water has been investigated both theoretically and experimentally. The theoretical modeling was conducted on the two reconstructed non-polar (111) and (110) surfaces of copper(I) oxide, using gradient corrected density functional calculations. Among the studied process steps related to the film growth were copper(I) chloride adsorption on different copper(I) oxide surface sites and reactivity against water. The experimental studies have been carried out from 350°C, where the films start to grow, up to 700°C, where the deposition rate starts to decrease. The texture of the films was controlled to a large extent by the substrates. On fused silica no texture was observed while on aluminium oxide, (102) oriented, films with strong (110) texture were obtained. The experimental results will be discussed in connection to the theoretical modeling of the deposition process.
- A/PIL.17** MECHANISM AND KINETICS OF HIGH-K ZIRCONIUM AND HAFNIUM OXIDE THIN FILM GROWTH IN ALD REACTOR
M. Deminsky(a,b), A.Knizhnik(a,b), I.Belov(a), S.Umanskii(a,c), E.Rykova(a,d), A. Bagaturiyants(a,d), B.V. Potapkin(a,b) and A.A. Korokin(e), (a)Kinetic Technologies, pl. Kurchatova 1, Moscow 123182, Russia, (b)Kurchatov Institute Russian Research Center, pl. Kurchatova 1, Moscow 123182, Russia, (c)Semenov Institute of Chemical Physics, Russian Academy of Sciences, ul. Kosygina 4, Moscow 117977, Russia, (d)Photochemistry Center, Russian Academy of Science, ul. Novatorov 7a, Moscow 117421, Russia, (e)Semiconductor Products Sector, Motorola Inc., 2200 W. Broadway Road, Mesa AZ 85202, USA
A kinetic mechanism of HfO₂ and ZrO₂ film growth in an ALD reactor is suggested to explain the following experimentally observed features of the process: (1) formation of less than 1 ML per cycle; (2) the film growth rate dependence on the degree of surface hydroxylation (that is, on temperature); and (3) the residual chlorine concentration dependence on process parameters. The mechanism is based on the results of quantum chemical calculations of surface reactions. The rate constants of elementary reactions were calculated using the RRKM theory. The calculated rate constants were used in ALD process simulations within the non-stationary surface plug-flow model. The effect of steric hindrances of the precursor ligands was analyzed using the kinetic Monte Carlo approach. This effect can be quite significant and lead to a decrease in surface coverage down to 30%. It restricts the steady-state film growth rate to about 0.4 ML/ALD cycle, which is in agreement with experimental data. It was found that surface dehydroxylation can significantly decrease the film growth rate. From the calculated kinetic curves, the lowest H₂O adsorption energy on the oxide surface below which the desorption of water molecules becomes significant was estimated at about 27 kcal/mol. The experimental dependence of the residual Cl concentration on the temperature can be explained by steric hindrances from surface groups to the chemisorption of MCl₄ molecules (M = Zr, Hf).
- A/PIL.18** ATOMIC LAYER CHEMICAL VAPOR DEPOSITION OF HAFNIUM AND ZIRCONIUM SILICATE THIN FILMS
Elizaveta Vainonen-Ahlgren, Eva Aro, Suvi Haukka and Marko Tuominen, ASM Microchemistry Ltd., P.O. Box 132, 02631 Espoo, Finland
So far the dominating insulator oxide in MOSFET devices and the dielectric in DRAM memory capacitors devices has been SiO₂. However, due to the shrinkage of the device structures pure SiO₂ will soon reach its fundamental limits. In order to continue making the devices smaller and smaller SiO₂ should be either modified with nitrogen or replaced with a material with a higher k-value. From the high-k materials HfO₂ and ZrO₂ are the most promising candidates today. Although they are quite thermally stable in contact with silicon at elevated temperatures there is still need for improvement. Furthermore the interface between the Si substrate and the high-k material has shown to play a key role in device performance. For these reasons Hf- or Zr-silicates have gained a lot of interest. In this study the ALCVD technique has been used to grow different type of hafnium and zirconium silicates. This method allows controlling the material thickness and quality due to layer-by-layer growth mechanism. The films were deposited on 200-mm Si (100) substrate. Both thickness and Hf/Si or Zr/Si ratio were varied. X-ray photoelectron spectroscopy, time-of-flight elastic recoil detection analysis and spectroscopic ellipsometry were used to determine the stoichiometry, impurities, thickness, and refractive index of the films.
- A/PIL.19** GROWTH DEFECTS W⁺²...W⁺³ IN CdWO₄ CRYSTALS.
N.V. Cherney, V.A. Nadolinny, A.A. Pavlyuk, Institute of Inorganic Chemistry, Novosibirsk, Russia
CdWO₄ crystals grown with Czochralsky method at low temperature gradient were investigated using ESR spectroscopy. ESR spectra missed the spectra of impurity ions typical for CdWO₄ structure, i.e. Fe⁺³, Mn⁺², Cr⁺³. At the same time in the studied crystals complex ESR spectrum having hyperfine structure due to two non-equivalent tungsten atoms was observed (W183, J=1/2, natural abundance 14.28%). Angular dependence analysis and simulation of ESR spectra have shown that this novel spectrum is described with spin-hamiltonian having parameters: D=839 G, E=69 G, g_{xx}=1.997, g_{yy}= 2.0, g_{zz}=1.987 and electron spin S=7/2. There is one magnetic non-equivalent position of center in the crystal structure and the direction of D_{zz} and g_{zz} corresponds to the direction of W_n...W_{n+2} (or Cdn...Cdn+2) in the crystal structure. Because of the fact that it is principally impossible to achieve electron state S=7/2 for d-shell of one transition metal ion and taking into account the fact that such electron state is realized for two non-equivalent tungsten atoms we suppose defect structure to be the chain W⁺² ... M⁺ ... W⁺³. In the structure of this defect the ion M⁺ is diamagnetic, the ions W⁺² and W⁺³ have electron spin S=2 and S=3/2 respectively. Needful condition of such defect existence is to place this chain of ions in cadmium positions for the charge compensation. The reason of such defects formation supposed to be the incorporation into the CdWO₄ lattice of M⁺ ions. The presence of W⁺² and W⁺³ in Cd positions in the defect structure provides the charge compensation and the lattice stress lowering.

- A/PII.20** RELATIVISTIC ELECTRONIC STRUCTURE OF THE REVERSIBLE REDOX COUPLES $[\text{Re}_6\text{S}_8\text{X}_6^{4+}/\text{Re}_6\text{S}_8\text{X}_6^{3+}]$, $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$
Ramiro Arratia-Perez(a) and Lucia Hernandez-Acevedo(b), (a)Facultad de Ecología y Recursos Naturales, Universidad Nacional Andrés Bello, Av. República 217, Santiago, Chile, (b)Av. Libertadores 405, El Monte, Region Metropolitana, Chile.
There is an increasing interest on the structure, optical and magnetic properties of some molecular forms of hexanuclear rhenium chalcogenide clusters, made up of $\text{Re}_6\text{Q}_8\text{L}_6$ ($\text{Q} = \text{S}, \text{Se}, \text{Te}; \text{L} = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{CN}^-, \text{pyr}, \text{etc.}$) cubic structures[1,2]. It has been recently known that these cluster ions display long emissive lifetimes (in the μs scale) with significant quantum yields, and undergo facile ground-and-excited state electron transfer, thus representing a novel class of rhenium-chalcogenide cluster photoreceptors for chemical reactions induced by light[1,3].
In this opportunity we present a series of Dirac molecular orbital calculations on each cluster component of the reversible redox couples (24e/23e): $[\text{Re}_6\text{S}_8\text{X}_6^{4+}/\text{Re}_6\text{S}_8\text{X}_6^{3+}]$, $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$. Here, we report self-consistent-field relativistic calculations on the ground state, excitation energies, density of states, cluster electronegativities, and the paramagnetic parameters (g, A_{hf}) of the oxidized 23e cluster ions[3,4]. An interesting set of conclusions are reached.
The reduced 24e cluster ions, which are luminescent, undergoes reversible oxidation processes at remarkably low potentials, thus indicating that they can easily be switched between two thermally stable oxidation states. So, they can store information and serve as molecular memory devices.
These unusual physical and chemical properties clearly suggest that these reversible redox couples could be part of suitable molecular nanocells for applications in molecular electronics and chemosensor nanodevices[1,4].
Acknowledgments: This research has been supported by Fondecyt N° 1000064 and the Direccion de Investigacion UNAB DI 62-A/99.
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- A/PII.21** COMPUTATION OF ELECTRON EMISSION IN INTERDIFFUSED Cr-Si LAYERS
A. Bouabellou, O. Belaissaoui, Laboratoire des Couches Minces et Interfaces, Université de Constantine, Campus Chaab Errassas, Constantine 25000, Algérie
The absolute values of the X-ray photoemission quantum yield are calculated in impulses at the K-absorption edge of the chromium atoms in thin chromium/chromium silicide/silicon layers in dependence on incidence angles of the X-ray beam on the photocathode and on films thicknesses. The contributions of all photoemitted electron groups are computed for various values of these parameters. At high energy excitation, the K-Auger electrons take control of the photoemission yield. The plotted curves show that the electron photoemission in Cr/Si system comes from a deepness of 1600 Å which is characteristic of the Cr K-Auger electrons depth. With increasing the incidence angle from 1,5 to 24°, the photoemission value decreases from 20% to 2,5%. For copper thicknesses lower than the maximum photoemission depth, the behaviour of the obtained curves is changed showing obviously the contribution of Si atoms in the electron emission. Also, the dependences of the photoemission jumps at K-edge on both chromium and chromium silicides layers thicknesses are established analytically. These curves, computed for Cr/CrxSiy/Si systems, can be used in the study of the growth kinetics of chromium silicides.
- A/PII.22** $\text{Fe}(\text{CO})_5 + \text{Fe}(\text{CO})_4 \rightarrow \text{Fe}_2(\text{CO})_9$ in a NANOSTRUCTURED DESIGN
Elena S. Apostolova, Department of Quantum Chemistry, D.I. Mendeleev University of Chemical Technology of Russia, Anatoly P. Tikhonov, College for Composite Materials, D.I. Mendeleev University of Chemical Technology of Russia
An ab initio study of $\text{Fe}(\text{CO})_4 + \text{Fe}(\text{CO})_5 \rightarrow \text{Fe}_2(\text{CO})_9$ (*) mechanism in the pre-reaction complex approach is reported. The method used is second-order Møller-Plesset theory using canonical orbitals (MP2) in the atomic basis set – Fe: (14s9p5d) / [10s8p3d]; C, O: (11s,6p)/[5s,3p]. We have predicted a new $\text{Fe}(\text{CO})_4$ conformer as the flat square (D4h) structure in the fundamental singlet electronic state [1], which bond energy BE 96.81 kcal/mol coincides well with the experimental one's 102.3 ± 10.5 kcal/mol. A structure of the pre-reaction complex of orbital controlling reaction (*), which is a first of reactions of born of new phase in materials contained Fe nanoparticles by $\text{Fe}(\text{CO})_5$ thermolysis, is discussed in terms of DFT reactivity indexes. Recommendations for the nanostructure synthesis are given.
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- A/PII.23** MODELLING OF DEFECTS AND EXCITED STATES IN NANOCCLUSERS AND AMORPHOUS OXIDES
P.V. Sushko, V.B. Sulimov and A.L. Shluger, Department of Physics and Astronomy, University College London, Gower St., London WC1E 6BT, UK
We developed an embedded cluster method to model systems, which cannot be easily treated using conventional molecular or periodic solid-state techniques. These include, for example, the structure and electronic properties of complex nano-clusters and powders, amorphous systems, electronically excited states (polarons and excitons), surfaces and dislocations, and materials under external mechanical and electric stress. The method is based on multi-scale modelling, which combines ab initio treatment of specific parts of the system under study with atomistic modelling of the remaining nano- or mesoscopic system using inter-atomic-potentials and shell model techniques. The key element in this approach is an embedding potential, which provides a link between the quantum and classical regions of the system. The results of ab initio calculations of defects and excited states in MgO nano-clusters and surfaces, and oxygen vacancies and self-trapped excitons in crystalline and amorphous silica demonstrate the vital role of the long-range defect-induced structural relaxation in determining the structure and electronic properties of these systems.

- A/PIL.24** ATOMISTIC SIMULATION OF DISLOCATION - GRAIN BOUNDARY INTERACTION IN A-IRON
D. Saraev, S. Schmauder, Staatliche Materialpruefungsanstalt (MPA) University of Stuttgart, Pfaffenwaldring 32, 70569 Stuttgart, Germany
The strengthening in polycrystals is the result of the restriction of dislocation motion due to the presence of grain boundaries. In this respect a detailed study of a dislocation - grain boundary interaction gains in great importance. In this work we present a nanoscale simulation of a moving edge dislocation interacting with a tilt grain boundary in iron by means of the Molecular Dynamics Method. The processes of dislocation glide, dislocation transfer and dislocation emission from grain boundaries are studied in detail. It is indicated that a dislocation transfer from one grain to another is strongly influenced by the orientation of the grains with respect to each other as well as by the applied stress. Depending on the misorientation of the grains, pile-up, transfer and the emission of dislocations have been observed. The effect of temperature on the dislocation - grain boundary interaction is discussed as well.
- A/PIL.25** WATER IN ZIRCONIA: DENSITY FUNCTIONAL MODELLING
J.L. Gavartin and A.L. Shluger, Department of Physics and Astronomy, University College London, Gower St., London WC1E 6BT, UK
Zirconia has wide applications as a refractive material, catalyst and as a material for fuel cells. It has recently attracted a lot of attention also as a prototype high-K dielectric. Water significantly affects the mechanical and electronic properties of zirconia and is known to be present in large quantities, e.g. in zirconia films grown on silicon. However, the microscopic mechanisms of water uptake by zirconia and the structure and stability of resulting species are poorly understood. We have modelled transformations of water in the bulk of monoclinic zirconia and calculated the electronic structure of resulting defect species. Our plane-wave density functional calculations suggest that water in zirconia dissociates into H⁺ and OH⁻ species, which incorporate into the lattice in the form OH⁻ centre in the oxygen lattice site and the interstitial OH⁻ molecular ion. These species have opposite charges with respect to the crystalline lattice, which results in their correlated migration with low activation energies. We discuss the mechanism of diffusion and the implications of the high mobility of the dissociated water on the mechanical and dielectric properties of zirconia. Vibrational frequencies of defect species are compared with the available FTIR data defect levels are determined with respect to the valence and conduction bands of silicon.
- A/PIL.26** THE EFFECT OF MOLECULAR PROPERTIES ON THE MESOSCOPIC BEHAVIOUR OF LUMINESCENT POLYMERS
Marta M.D. Ramos, A.M. Almeida, Helena M.G. Correia, R. Mendes Ribeiro, Departamento de Física, Universidade do Minho, Largo do Paço, 4700-320 Braga, Portugal and A.M. Stoneham, Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK
The electrical and optical properties of luminescent polymers, such as poly(p-phenylene-vinylene) (PPV) and polydiacetylene (PDA), depend both on the properties of individual polymer strands and on polymer chain arrangement. Therefore, energy and spatial molecular disorder have a serious influence on migration of charge carriers within the polymer layer. The transfer of carriers between two polymer chains will depend on the chemical potential difference as well as on other features such as the distance between both molecules involved and the direction of the electric field. The purpose of the present work is to clarify the effects of local energy and polymer structural disorder on current flow, trapping and recombination on polymer based devices, using a generalised Monte Carlo method. In addition, for the evaluation of bipolar charge transport in polymer networks, different molecules are considered to have different energy parameters, since the chemical potential of a particular polymer depends on the length and curvature as well as on the molecular charge. The intra-molecular electronic properties were characterised by a quantum molecular dynamics method. The difference between steady state and pulse operation is also considered. Our results suggest that the competition between current flows, trapping and recombination often lead to unexpected behaviours.
- A/PIL.27** MONTE CARLO SIMULATIONS STUDY OF THE PHASE DIAGRAMS OF 3-DIMENSIONAL LATTICE-GAS MODELS OF WATER-SURFACTANT-OIL EMULSIONS
R. Valente, A.M. Cadilhe and M.D. Ramos, Centro de Física do Departamento de Física da Universidade do Minho, 4710-057 Braga, Portugal
We present preliminary results of the phase diagram of suitable 3-dimensional lattice-gas models. Specifically, we performed Monte Carlo simulations of a two-state model and compare the results with a three-state lattice-gas model. We use Kawasaki-type, conserved order parameter dynamics to identify the critical points. Surfactant molecules have a hydrophobic tail and a hydrophilic head, which causes them to preferentially seat at the interface water-oil, and thus substantially reduce the interfacial energy between water and oil. Due to the large computational effort required in these 3-dimensional models, we focus on the micellar phase and on the microemulsion phase. We characterize both the location of the critical points and the structure of these phases.

- A/PIL.28** FIRST PRINCIPLE INVESTIGATION OF WATER ADSORPTION ON ZIRCONIA AND HAFNIA SURFACES
I. Iskandarova(a,b), A.A. Knizhnik(a,b), A.A. Bagaturiyants(a,c), B.V. Potapkin(a,b) and A.A. Korkin(d), (a)Kinetic Technologies, pl. Kurchatova 1, Moscow 123182, Russia, (b)Kurchatov Institute Russian Research Center, pl. Kurchatova 1, Moscow 123182, Russia, (c)Photochemistry Center, Russian Academy of Science, ul. Novatorov 7a, Moscow 117421, Russia, (d)Semiconductor Products Sector, Motorola Inc., 2200 W. Broadway Road, Mesa AZ 85202, USA
The degree of hydroxylation of ZrO₂ and HfO₂ surfaces is the factor determining both the film growth rate of the corresponding oxides in the ALD process and the surface chemical properties of the deposited films. The adsorption energy depends on the surface hydroxylation, and can affect the character of adsorption (dissociative vs. molecular) The aim of this work was to determine the adsorption energy of a water molecule on various ZrO₂ and HfO₂ surfaces as a function of surface coverage. We considered the (001) and (101) surfaces of tetragonal ZrO₂ and (001) surface of monoclinic HfO₂. Calculations were carried out using the plane-wave GGA DFT method. The properties of the bulk phases and the corresponding surface energies were calculated and compared with available experimental data. The adsorption energies of a water molecule were calculated for 100%, 75%, 50%, and 25% surface coverage on the (001) surface of t-ZrO₂ and for 100% and 50% coverages on others surfaces. It was found that the adsorption energies of water molecule at 100% surface coverage were relatively small for both the dissociative and molecular forms (e.g., for the (001) surface of t-ZrO₂, these energies were < 50 kJ/mol. Based on our results and available experimental data, we concluded that 50% surface coverage is a maximum that can be reached under typical ALD process conditions.
- A/PIL.29** QUANTUM-CHEMICAL STUDY OF THE MECHANISM OF HfO₂ ATOMIC LAYER DEPOSITION FROM HfCl₄ AND H₂O PRECURSORS
E.A. Rykova(a,b), A.A. Knizhnik(a,c), A.A. Bagaturiyants(a,b) and A.A. Korkin(d), (a)Kinetic Technologies, pl. Kurchatova 1, Moscow 123182, Russia, (b)Photochemistry Center, Russian Academy of Science, ul. Novatorov 7a, Moscow 117421, Russia, (c)Kurchatov Institute Russian Research Center, pl. Kurchatova 1, Moscow 123182, Russia, (d)Semiconductor Products Sector, Motorola Inc., 2200 W. Broadway Road, Mesa AZ 85202, USA
The mechanism of HfO₂ ALD from HfCl₄ and H₂O precursors on a Si(100) substrate was studied using DFT. Cluster calculations were performed for models of the unoxidised an oxidized Si(100)-2x1 surface. The reaction of HfCl₄ with OH-terminated fully oxidised and unoxidised Si(100)-2x1 surfaces, surface reaction between chemisorbed HfCl₃ and OH groups, and the hydrolysis of chemisorbed HfCl₂ groups were considered as initial HfO₂ ALD steps. It was shown that the interfacial SiO₂ layer is favourable for film deposition and that HfO₂ ALD must proceed easier and at lower temperatures than ZrO₂ ALD, which agrees well with the available experimental data. To provide an insight into the steady-state mechanism of HfO₂ film growth and explain temperature effects, the hydroxylation-dehydroxylation reaction on the most rapidly growing m-HfO₂(001) surface was studied using periodic plane-wave and cluster DFT calculations. The periodic calculations were performed with the PBE nonlocal exchange-correlation functional using a four-layer slab model. Cluster calculations were performed using embedded Hf₃O₁₄ and Hf₆O₂₄ clusters. The results of periodic and cluster calculations suggest that the hydroxylation-dehydroxylation step determines the kinetics of HfO₂ ALD at high temperatures.
- A/PIL.30** EMBEDDED CLUSTER CALCULATIONS OF OXYGEN VACANCIES IN THE BULK AND AT THE SURFACE OF TETRAGONAL ZrO₂
A.A.Safonov(a,b), A.A. Bagaturiyants(a,b) and A.A. Korkin(c), (a)Kinetic Technologies, pl. Kurchatova 1, Moscow 123182, Russia, (b)Photochemistry Center, Russian Academy of Science, ul. Novatorov 7a, Moscow 117421, Russia, (c)Semiconductor Products Sector, Motorola Inc., 2200 W. Broadway Road, Mesa AZ 85202, USA
Formation of oxygen vacancies in t-ZrO₂ was studied using ab initio embedded cluster calculations. The vacancy formation energies were calculated, and the activation energy of vacancy migration was determined for bulk t-ZrO₂. Clusters were surrounded with Zr⁴⁺ pseudopotentials located at crystal lattice sites and embedded in the Coulomb field of (+4/-2)point charges modelling. The set of point charges was constructed using a new procedure specially developed to improve the accuracy of the potential. At optimized geometries, the energies were calculated by the B3LYP method, and the basis sets of the central O atoms were replaced with 6-311G*. The LANL1 effective core potentials without basis sets were used for the Zr⁴⁺ pseudopotential environment. The energy of oxygen vacancy formation in bulk t-ZrO₂ was found to be 8.8 eV for the process yielding a free O atom and 6.1 eV for the process yielding an O₂ molecule. The barrier for oxygen vacancy migration in bulk t-ZrO₂ was found to be 1.9 eV. The formation energy of oxygen vacancy at the (001) surface of t-ZrO₂ was 6.6 and 3.9 eV for the formation of atomic and molecular oxygen, respectively.
- A/PIL.31** A ROLE FOR DINUCLEAR ALUMINIUM AMIDINATE COMPLEXES IN ETHYLENE POLYMERISATION?
Robert J. Meier, DSM Research, P.O.Box 18, 6160 MD Geleen, The Netherlands
Aluminium amidinate species, found active in ethylene polymerization, have been studied using a variety of computational methods, including semi-empirical (AM1), Hartree-Fock and Density Functional Theory type calculations, and first principles MD simulations. In agreement with experimental observations, we find that for all pairs of experimentally studied substituents, the larger dinuclear amidinate structures are very stable toward decomposition. However, with respect to the structure of the active ethylene catalyst, for the most stable dinuclear structures sterically crowding substituents inhibit insertion through a very high energy barrier, whereas for non-crowding systems chain termination by β -hydrogen transfer is likely to dominate over insertion. From finite temperature dynamics simulations we observe strong fluctuations in the length of the bond bridging the two amidinate rings in one of the dinuclear structures. Lengthening of that bond relaxes the steric constraints, lowering the barrier for insertion, while still forcing the growing alkyl chain to adopt an orientation which inhibits rapid chain termination. Thus, effects explicitly related to finite (non-zero) temperature seem necessary to account for the catalytic activity of these amidinates. This study clearly indicates that it is necessary to model the real catalyst, including bulky substituents if present, to arrive at a proper understanding of structure and reactivity.

A/PIL.32

FRACTAL DESCRIPTION OF CLUSTERS FORMED IN THE THIN FILMS GROWTH SIMULATIONS

K. Zembrowska, L. Pyziak, M. Kuzma, I. Stefaniuk, Institute of Physics, University of Rzeszow, Rejtana 16A, 35-959 Rzeszow, Poland

The first Si monolayer growing on Si (001) substrate by pulsed laser deposition method (PLD) was simulated using Monte Carlo procedure. A various growing conditions like, temperature of substrate, energy of adatoms, etc. were introduced into simulation. The shape of clusters formed depends on these conditions clearly. The best method for description of cluster shape is they fractal characterisation. Box fractal dimension of these planar objects was studied. This parameter selects very well the shape of such clusters, which are most favourable for the epitaxial layer-growing mode. The relation between the fractal dimension of clusters and PLD parameters was established.

A/PIL.33

AB INITIO STUDIES OF THE INTERACTION BETWEEN A DIMERCAPTOACETOAMIDOBENZENE MOLECULAR WIRE AND DERIVATIVES AND Au₁₃ NANOCCLUSERS

M. Nolan, J.A. Larsson, and J.C. Greer, NMRC, Lee Maltings, Prospect Row, Cork, Ireland

This work presents the results of density functional theory studies of the interaction between an organic molecular linker, dimercaptoacetoamidobenzene (DMAAB), and a "magic number" gold cluster. Bonding between two gold nanoparticles, changing the conformation of the linker molecule and the effect of chemical substitution in the linker are assessed through considering the resulting interfacial geometry and electronic structure of the metal-linker-metal complex. Bonding of the molecular wire between two gold clusters leads to a bond elongation similar to that found for the case of bonding to a single metal cluster, and results in little modification to the electronic structure of the linker. Conformational effects lead to a significant change in the geometry in the interfacial region and as well to the electronic structure of the metal-linker-metal complex. Chemical substitution in the molecular wire does not affect the interfacial geometry, but has a large effect on the electronic structure. Energy level shifts are particularly strong for those orbitals derived from the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the free molecule. The charge distributions in the molecule are also strongly affected. We discuss the effect of the conformational and substitutional changes in terms of the energy level alignments in the metal-linker-metal complex.

Symposium A

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Session VII: CVD & Growth

- 09:00 **A-VII.1** **QUANTUM MONTE CARLO CALCULATIONS OF HYDROGEN ADSORPTION ON Si(100)**
Claudia Filippi, Instituut-Lorentz, Universiteit Leiden, The Netherlands
The Si(100) surface has become a paradigmatic system to test our general understanding of surface physics and chemistry. Despite extensive experimental and theoretical investigation, fundamental aspects of the interaction of molecular hydrogen with the Si(100) surface are still subject to debate. We revisit the topic using large model clusters of the surface and quantum Monte Carlo techniques to accurately account for electronic correlations. Our calculations predict reaction energies and barriers significantly higher than approximate density functional theory calculations. The higher adsorption barriers are in better agreement than previous DFT results with the observed low sticking coefficient of H₂ on Si(100). Various adsorption/desorption mechanisms will be discussed.
- 09:40 **A-VII.2** **FROM SILICON OXIDE TO HIGH-K DIELECTRICS: A CHALLENGE FOR COMPUTATIONAL MATERIAL SCIENTISTS**
Gennadi Bersuker and Howard R. Huff, International SEMATECH, 2607 Montopolis Dr., Austin, TX 78741, USA
Aggressive device scaling calls for gate dielectrics with smaller effective oxide thickness, down to 1 nm and even 0.5 nm, and raises concerns about their reliability. Extensive research efforts to identify the key factor controlling electrical properties of SiO₂ films have not yet yielded a comprehensive model, while our understanding of the high-k materials is even further away. Modeling efforts, which target experimentally well-defined issues, are essential for speedy progress.
Ab initio calculations of the bulk and interfacial layer of SiO₂ have identified the localized states in the oxide band gap associated with oxygen-related defects. Electron capture by these states were shown to lead to Si-O bond breakage and eventually the generation of paramagnetic E'centers. This scenario for oxide degradation phenomenon in the direct tunneling regime found support in accelerated electrical stress measurements. Leakage currents in high-k films (ZrO₂, HfO₂, and their silicates) were also attributed to electrically active localized states; these states were calculated to be induced by metal ions in conjunction with oxygen vacancies and oxygen interstitials. However, the range of experimental effects of great practical importance are yet largely un-addressed and ripe for modeling explorations.
- 10:00 **A-VII.3** **STUDY OF SILICON NANO-CLUSTER SELF-LIMITING OXIDATION BY ATOMISTIC SIMULATIONS**
J. Dalla Torre, J.-L. Bocquet, Y. Limoge, J.-P. Crocombette, E. Adam, G. Martin, CEA Saclay, SRMP, Gif-sur-Yvette, France, T. Baron, LTM, Grenoble, France, P. Rivallin, P. Mur, CEA Leti, SRD, Grenoble, France
Oxidation of silicon nano-spheres or -cylinders is known to develop stresses that yield a self-limiting oxidation behavior which is of practical interest. It may be used to control the size and the size distribution of a cluster assembly, of importance e.g. in quantum dots based single electron devices. Stress is expected to affect the oxide formation energy, the oxidant diffusion or reaction at the silicon/oxide interface.
We study the silicon oxidation by molecular dynamics simulations using an extended Stillinger-Weber interatomic potential for Si, O mixed systems developed by Watanabe and co-workers. Oxygen atoms are directly inserted in the Si-Si bonds to form the silicon oxide.
Using this technique, we can compute the local stress in the system as the oxide grows. We tested first the model on the oxidation of flat Si substrates. Next, the oxidation of spherical clusters is presented. We show that continuum models fail to give the correct evolution of stresses as a function of the oxide shell thickness and that pressure variations through the oxide shell can have large effects on the oxidant transport to the Si nucleus.
- 10:20
- 10:40 **A-VII.4** **GROWING CONTROLLED NANOCUSTER FILMS**
Pablo Jensen, Département de Physique des Matériaux, UMR CNRS 5586, Université Claude Bernard Lyon-1, 69622 Villeurbanne Cedex, France
I will present recent results on the growth of nanostructured films prepared by cluster deposition. After the surprisingly high values for cluster diffusivity found on graphite surfaces, we investigated cluster diffusion on a variety of different substrates, to understand technologically important experimental issues. The simulation results are compared to experiments.

Symposium A

- 11:20 **A-VII.5** **AB INITIO MODELLING OF OXYGEN DEFECTS IN GATE OXIDES**
A.S. Foster, V.B. Sulimov, P.V. Sushko, F. Lopez Gejo, A.L. Shluger and R. Nieminen, Laboratory of Physics, Helsinki University of Technology, P.O. Box 1100, 02015 Helsinki, Finland and Department of Physics and Astronomy, University College London, Gower St., London WC1E 6BT, UK
Modelling of point defects induced by growth and subsequent annealing of oxide films is important for their applications as gate oxides. Using periodic plane wave DFT and embedded cluster methods we have studied the structure and electronic properties of neutral and charged oxygen defects in three prototype gate oxides: monoclinic ZrO₂ and HfO₂, and amorphous SiO₂. The structure, ionisation energies and electron affinities of oxygen vacancies and interstitial oxygen atoms and molecules in different charge states were calculated. The positions of defect levels with respect to the bottom of silicon conduction band are determined. The results demonstrate that interstitial oxygen atoms and molecules, and positively charged oxygen vacancies can trap electrons from silicon. Diffusion mechanisms of oxygen species and vacancies are analysed and their role in degradation of gate oxides is discussed.
- 11:40 **A-VII.6** **HETEROEPITAXIAL GROWTH OF HIGH-K GATE OXIDES ON SILICON: INSIGHTS FROM FIRST-PRINCIPLES CALCULATIONS**
Clemens J. Först(a,b), Peter E. Blöchl(a) and Karlheinz Schwarz(b), (a)Institute for Theoretical Physics, Clausthal University of Technology, Leibnitzstraße 10, 38678 Clausthal-Zellerfeld, Germany, (b)Institute for Material Chemistry; Vienna University of Technology, Getreidemarkt 9, 1060 Vienna, Austria
Scaling of semiconductor devices currently results in structures with nearly atomic dimensions. Gate oxides, which separate the switching current from the drive current in a MOSFET transistor, are approaching a thickness range of only few atomic layers, so that quantum-mechanical leakage currents become intolerable. New insulating materials with larger dielectric constants, e.g. high-k oxides, can be implemented at a larger physical thickness with electrical properties equivalent to those of an ultrathin conventional gate oxide. We present the results from ab-initio molecular dynamics simulations using the projector augmented wave method on the heteroepitaxial growth of high-k oxides on silicon.
- 12:00 **LUNCH**

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Afternoon
Après-midi

Session VII: CVD & Growth

- 14:00 **A-VII.7** **THEORY OF THE PHASES AND ATOMISTIC STRUCTURE OF YTTRIA-DOPED ZIRCONIA**
S. Ostanin, E. Salamatov, A. Craven, D. McComb, A. Alavi, A.T. Paxton, M. Finnis, Department of Physics, University of Warwick, Coventry CV4 7AL, UK, Physico-Technical Institute, Ural Branch of RAS, Izhevsk 426001, Russia, Department of Physics, University of Glasgow, Glasgow G12 8QQ, UK, Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, UK, Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, UK, School of Mathematics and Physics, Queen's University, Belfast BT7 1NN, UK
The electronic structure of yttria-stabilised zirconia for compositions between 3 and 15 mol % yttria has been computed using a pseudopotential based technique to calculate the local relaxations near the O vacancies. The phase transition from the tetragonal to cubic phase predicted at 10 mol % yttria reproduces experimental observation. Using the relaxed defect geometry, calculation of the electron energy-loss near-edge structure (ELNES) was carried out using the full-potential linear muffin-tin orbital method. The results show very good agreement with the experimental O K-edge signal, demonstrating the power of using ELNES to probe the stabilization mechanism in doped metal oxides. In the displacive limit of the double-well potential model, the vibration mode corresponding to the soft phonon in pure cubic zirconia has been calculated for each composition of yttria. These anharmonic vibrations were investigated within the self-consistent phonon approximation making obtainable the fine structure in spectral density. The displacement probability density calculated can quantify very accurately the transition temperature necessary for stabilizing the cubic phase.
- 14:20 **A-VII.8** **RANSPORT LIMITATION EFFECTS OF ATOMIC LAYER DEPOSITION IN HIGH ASPECT RATIO STRUCTURES**
A. Kersch, G. Schulze-Icking, Infineon Technologies AG, Memory Products, Balanstrasse 73, 81541 Munich, Germany
One possible cause for non-ideal ALD growth are insufficient cycle times which can result in an unsaturated surface coverage, at least at some positions of a microscopic structure. We have developed a Monte-Carlo transport simulation technique coupled to a feature scale simulator to investigate the time evolution of surface coverages during the ALD deposition step. For different precursor sticking coefficients and for structures with different aspect ratios we have calculated the minimal time required to reach complete surface saturation. Furthermore we have calculated the front of the grown film after several cycles. Our results clearly indicate that for extreme aspect ratios the cycle frequency may be limited by the gas transport inside the feature. This effect has so far been neglected but needs to be taken into account for future ALD process and equipment developments for DT processes.
- 14:40 **A-VII.9** **AB INITIO INVESTIGATION OF BASIC MECHANISMS DURING HfO₂ DEPOSITION ON Si**
Leonard Jeloica, Alain Esteve, Daniel Esteve, LAAS-CNRS, 7 av. du Colonel Roche, 31077 Toulouse, France, Mehdi Djafari Rouhani, Laboratoire de Physique des Solides, 118 route de Narbonne, 31062 Toulouse, France
Use of high-k dielectric materials has been suggested in MOS transistor gates, as an alternative to SiO₂. The advantage is thicker films, reducing simultaneously the tunnel current and the gate voltage. However, in practice, the performances of the devices are greatly reduced because of the presence of defects in the deposited films and the consequent reduction of the dielectric constant. A proper modeling of the mechanisms involved during deposition seems therefore necessary for an adequate design of the process. We are interested in HfO₂ which is one of the potential candidates. Our objective is to develop a multi-scale modeling associating ab initio results with a Monte Carlo simulation.
In this paper, we focus mainly on the ab initio investigation of chemical reactions between the substrate and the precursor molecules in the gas phase, used in the atomic layer epitaxy process. Several types of precursors and different surface configurations have been tested. The energies associated with these configurations will be discussed in order to determine the reaction paths and to estimate the corresponding energies.