SYMPOSIUM E

Nucleation and Growth Processes in Materials

November 29 – December 1, 1999

Chairs

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* Invited paper

8:30 AM *E1.1
ROLE OF ACTION PRINCIPLES IN MICROSTRUCTURE
FORMATION. John S. Kirkaldy, Brockhouse Institute for Materials
Research, McMaster University, Hamilton, Ontario, CANADA.

A modification of Hamilton's action principle from classical
mechanics, where the Lagrangian is generalized to frictional systems,
is thermodynamically adapted to the dissipative, isothermal heat
bath-enclosed condensed state. This reveals stable stationarity of the
dissipation rate at the steady or quasi-steady state and a fully
time-dependent action principle based upon the free energy density
form of the Laplacian density, with the time-dependent
Ginzburg-Landau equation as Euler-Lagrange equation. In this
formalism it is the group theoretical symmetry of the Lagrangian
density which, as a consequence of Noether's Theorem, determines the
conservation laws rather than any extraneously applied continuity
principle. When such are nonetheless applied the resulting partial
differential equations harbour an overdetermination. The approximate
equivalence of Hillert's atomistic approach to the kinetics of spinodal
and order-disorder decomposition through Bragg-Williams
thermodynamics and Prigogine's chemical reaction kinetics is
illustrated. This result is generic with model calculations relying on
Master Equation or Path Probability approaches to the same
problems. The implications for the descriptions of grain growth,
Ostwald Ripening and steady state spinodal decomposition are
examined.

9:00 AM *E1.2
EVOLUTION OF MULTIPHASE MULTIVARIANT COHERENT
SYSTEMS DRIVEN BY STRAIN ACCOMMODATION.
Armen G. Khachaturyan, Rutgers University, Piscataway, NJ; Yann
Le Bouar, CEA Saclay, Gif Sur Yvette, FRANCE; Andrei Artemev,
Carleton University, Ottawa, Ontario, CANADA.

The coherent transformation whose crystal lattice rearrangement has
the point symmetry that is lower than the symmetry of the parent
phase produces several orientation variants of the product phase.
Spatial patterns formed by multivariant domains of the product phase
are determined by the coherency strain. They actually are elastic
domain structures, which in many respect are similar to the magnetic
and ferroelectric domain structures. The Phase Field Micromechanics
of structurally inhomogeneous systems developed by one of the
authors allows us to formulate the Phase Field Theory that explicitly
incorporates strain with practically no computational cost. The
theory is effective for a realistic 3-D computer simulation of the
microstructure formation with the arbitrary crystal lattice
rearrangement. The 3-D computer simulations of the coherent
transformations indicate that this approach is a powerful tool for
virtual reality prototyping the real processes. It provides excellent
qualitative and quantitative agreement with fine details of the
observed microstructure and is able to predict how the microstructure
depends on the processing parameters. The input parameters of the
computer simulations are not fitting parameters to obtain the
agreement between the observation results. They are taken from
independent measurements unrelated to the properties that are
simulated. Research is supported by NSF grant DMR 98-17235

9:30 AM E1.3
PHASE COARSENING AS A RELAXATION PHENOMENON.
Steven P. Marsh, Naval Research Lab, Washington, DC.

Phase coarsening, also known as Ostwald ripening, is generally
treated as a growth phenomenon in which the average particle size
increases during isothermal aging. However, coarsening is a relaxation
process driven by a reduction in the excess interfacial energy of a
two-phase structure. This viewpoint introduces a single temporal
offset parameter that relates the experimental clock to the asymptotic
time scale. Analysis of ripening as a relaxation phenomenon permits
accurate determination of the kinetics that is less sensitive to particle
morphology. Implications of this approach on measurement and
interpretation of ripening kinetics will be discussed.

9:45 AM E1.4
ADVANCE IN PHASE FIELD APPROACH FOR MICRO-
STUCTURAL EVOLUTION WITH THE PRESENCE OF FREE
SURFACE AND GRAIN BOUNDARY: INCORPORATION OF
RIGID-BODY MOTION. Chen Shen and Yunzhi Wang, Department
of Materials Science and Engineering; Andrei Kanzayan and Bruce R.
Patton, Department of Physics, The Ohio State University, Columbus,
OH.

A complete theoretical description of microstructural evolution with

the presence of free surface and grain boundary requires a treatment
that incorporates not only multiple diffusion paths but also rigid-body
motion of the solid particles. In this presentation we describe a
generalized phase field model which incorporates rigid-body motion
together with different diffusion mechanisms. This advance allows
different phenomena occurring during the microstructural evolution to
be simulated in a single, consistent methodology. Simulation results
for the evolution of pores at grain boundary and the densification
kinetics with the absence and presence of an externally applied force
will be discussed in the light of available analytical and numerical
data. Different strategies for the incorporation of the rigid-body
motion will be discussed.

10:30 AM *E2.1
A NEW MICROSCOPIC KINETIC APPROACH FOR ALLOYS.
Maylise Nastar, Georges Martin, CEA Saclay, SRMP, Gif-sur-Yvette
Cedex, FRANCE.

We present a new set of self-consistent mean-field equations for
describing the kinetics of phase transformations in alloys. For the
specific case of a vacancy diffusion mechanism, the latter kinetic
equations are shown to reproduce the correlation effects which are not
included in the other mean-field theories. The derivation is based on
the master equation which provides the time evolution of the
distribution function of the system. The zero-order self consistent
approximation consists in considering the time evolution of only the
first and second moments of the distribution function, the time
evolution of the higher order moments are expressed in terms of these
first and second moments. These expressions depend on the
configurational Hamiltonian pairwise interactions, the attempt jump
frequencies and the alloy composition. Simulation of kinetics of grain
boundary segregation after annealing are presented and comparisons
with other mean field theories are discussed.

11:00 AM *E2.2
COHERENCY STRAIN INDUCED ORDERING IN SUBSTI-
TUTIONAL ALLOYS. J.K. Lee[1], M. Hiratani[2], K. Kalaitzidou[3] and
A. Shyam[1], Departments of Metallurgical and Materials Engineering[1],
Physics[2], and Mechanical Engineering and Engineering Mechanics[3],
Michigan Technological University, Houghton, MI.

It has been well known that one of the driving forces for ordering is
the relaxation of elastic strain energy due to difference in atomic size,
a clear evidence being the change in lattice parameter between
ordered and disordered states. Because of mathematical complexity,
however, no stress model appears to have been presented for
substitutional alloys. In this work, we report coherency-induced
ordering in a simple model with a square lattice. At an equi-atom
composition, a square lattice displays two ordered structures, $S1_0$ and
$S1_1$, similar to $L1_0$ (CuAuI) and $L1_1$ (CuPt) in fcc. The stability of
the two superlattices at the ground state depends strongly on elastic
anisotropy. For a homogeneous system, i.e., if the elastic constants of
both solvent and solute elements are the same, Zener's anisotropy
ratio is sufficient to measure the stability of one structure against the
other. If the elastic constants are different, however, the stability
depends not only on the elastic moduli of both elements but also on
the solvent-solute bond length. The order-to-disorder transition is
studied via the discrete atom method, which is predicated upon
statistical mechanics and linear elasticity. Near the transition
temperature, the long range order shows somewhat greater
fluctuations than its counterpart in a conventional quasichemical
model. When both elastic and chemical interactions join together for
ordering, the transition temperature is raised to a value greater than
the sum of the two transition temperatures from each of the individual
cases – an indication of a coupling between the two driving forces.

11:30 AM E2.3
PHASE SEPARATION AND ELASTIC FIELDS:
THREE-DIMENSIONAL SIMULTIONS OF A PHASE FIELD
MODEL. Celeste Sagui, Daniel Orlikowski, Department of Physics,
NC State University, Raleigh, NC; Andres Somoza, Departamento de
Fisica, Universidad de Murcia, Murcia, SPAIN; and Christopher
Roland, Department of Physics, NC State University, Raleigh, NC.

The process of phase separation for quenched three-dimensional
binary alloy systems with coupled elastic fields was investigated via
the numerical integration of a phase field model. The elastic fields,
which are the result of anisotropy and dilational misfits introduced
via inhomogeneities in the elastic constants of the constituents,
profoundly effect the domain morphology and growth mechanisms

observed. The growth morphology can be understood in terms of a selection criterion which is formulated in terms of the different effective shear moduli of the system. This criterion enables one to determine the phase, the shape and the orientation of the resulting domain structures. The coarsening behavior of the elastically strained system involves both a modified Ostwald ripening and transient coalescence phenomena, and is understood in terms of effective chemical potential barriers surrounding the precipitates. Evidence for dynamic scaling in both the structure factor and cluster distribution functions, along with inverse coarsening effects, will also be presented.

11:45 AM <u>E2.4</u>
STEADY STATE COMPOSITIONAL PATTERNING IN ALLOYS UNDER IRRADIATION. <u>Raúl Enrique</u> and Pascal Bellon, University of Illinois, Dept. of Materials Science and Engineering and Materials Research Laboratory, Urbana, IL.

It is well known that an alloy subjected to an external irradiation flux can suffer changes in the stability of the existing phases, as well as changes in its microstructural features. For certain irradiation conditions (replacement collision sequences, low energy ion irradiation), these changes arise from a competition between the atomic mixing produced by an irradiation event and the thermally-driven kinetics. Under this competition, the alloy eventually reaches a steady state away from thermal equilibrium, which is a function of both the frequency and characteristics of the irradiation. In binary alloys with positive heat of mixing, regardless the range of mixing in each irradiation event, enhancement solubility in the terminal phases is observed, both in simulations and experiments. Microstructural changes in these alloys, however, are sensitive to the characteristics of the irradiation. Very short replacement collision sequences produce a similar microstructure to that of equilibrium, although a change in the relative stability of different interface orientations is observed. In the limit of very long range replacements, on the other hand, the formation of labyrinthine compositional patterns is observed. We study the steady-state microstructural changes as the range of the atomic mixing due to irradiation is varied. We observe in certain cases the formation of steady-state patterns with definite lengths, even for finite-range replacements. The results are rationalized by appealing to *effective thermodynamics* formulations, where long-range repulsive effective interactions appear. Stability analysis of a discrete version of the Cahn-Hilliard equation, where we maintain all high-order derivative terms, also helps to explain the nature of these structures. In experimental situations, these results suggest that control of the irradiation parameters can be used as a mean to either favor or avoid pattern formation.

SESSION E3: PHASE TRANSFORMATIONS III
Chair: Gernot Kostorz
Monday Afternoon, November 29, 1999
Room 210 (H)

1:30 PM <u>*E3.1</u>
ACCURATE ANALYTICAL METHODS FOR STATISTICAL-THERMODYNAMIC DESCRIPTION OF ALLOYS).
<u>Volodymyr N. Bugaev</u>, Inst for Metal Phys, Dept of Solid State Theory, Kiev, UKRAINE.

Due to the essentially long-range character of realistic atomic interactions, the universal shortcoming of all 'real-space' statistical-thermodynamic methods arises at the description of actual materials. For instance, it is known that, due to the strain-induced effects caused by the impurity atoms in a host lattice, the nonanaliticity of the Fourier component for effective pair atomic interchange potential takes place. This makes the 'real-space' consideration to be incorrect when taking into account atomic interaction within only the finite number of coordination shells. Recent success in the equilibrium statistical-thermodynamic description of atomic lattice systems is connected with the development of the 'reciprocal-space' Ring approximation (J. Phys.: Condens. Matter, 10, 33, 7309, 1998; Ibid., 7327, 1998) within the thermodynamic perturbation theory. The high accuracy of the Ring approximation in comparison with the mostly used analytical ones is ascertained in the cases of model systems and real alloys. It is shown, that the important advantage of the Ring-type approach is the potential of taking into account the many-body contributions into atomic interactions and the possibility of study not only the binary but also the multicomponent materials without the essential complication of a consideration. Using the Ring-type approach, the semi-phenomenological microscopic nsager equation technique is adapted for the description of the diffusion controlled processes which occur in material within the atomic ranges (spinodal decomposition, long- and short-range order kinetics).

2:00 PM <u>*E3.2</u>
A DICTRA$^\oplus$ SIMULATION OF Θ DISSOLUTION IN Al-Cu ALLOYS. <u>Raymond G. Thompson</u>, Research Professor, University of Alabama in Birmingham; and Curt Malam, University of Alabama in Birmingham, Birmingham, AL.

The dissolution of micron-sized Θ in Al-Cu alloys has been studied extensively using various experimental techniques. The literature contains studies of both mono-sized particle dissolution and the dissolution of a distribution of particle sizes. The dissolution of particles is important to many materials processing operations. The ability to simulate and model the precipitate dissolution would be of significant technical value. Computational methods for thermodynamic and microstructure modeling offer such opportunities. This paper presents the results of a DICTRA$^\oplus$ simulation of q particles in Al-2Cu and Al-4Cu alloys. The simulation conditions were chosen to mimic the experimental conditions found in the literature on Θ dissolution in Al-Cu alloys. The results from the simulation were compared to the experimental results found in the literature. The general findings were that the simulations gave results that accurately represented the experimental findings. There is some evidence that the simulations gave results that were more accurate than the experiments due to inherent errors expected in the experimental measurement of sub-micron particles.

2:30 PM <u>E3.3</u>
CHARACTERIZATION OF THE EARLY STAGES OF PHASE SEPARATION BY ATOM PROBE TOMOGRAPHY. <u>M. K. Miller</u>, Microscopy and Microanalytical Sciences Group, Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN.

Atom probe tomography provides a unique real space experimental tool to characterize the earliest stages of phase separation in metal systems. In the three-dimensional atom probe, the x, y, and z coordinates and the mass-to-charge ratio and hence the identity of the atoms in a small volume may be determined with near atomic precision. From this information, the size, shape and composition of ultrafine features such as embryos and precipitates may be characterized. The early stages of decomposition have been characterized in an Fe- 1.1% Cu $\sim$1.4% Ni model alloy. The development of the copper-enriched regions into copper precipitates has been determined during isothermal ageing at 573 K and 673 K for times up to 10,000 h. In addition, the formation and growth of the secondary precipitates in the complex nickel based superalloy, Alloy 718, have been determined during isothermal ageing at 873 K. These secondary precipitates were found to be a mixture of the L12-ordered phase and the DO22-ordered phase. This research was sponsored by the Division of Materials Sciences, U. S. Department of Energy, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp. This research was conducted utilizing the Shared Research Equipment (SHaRE) User Program facilities at Oak Ridge National Laboratory.

2:45 PM <u>E3.4</u>
INTERDIFFUSION MICROSTRUCTURE MAP TOPOLOGY. F. Meisenkothen, Department of Materials Science and Engineering, Ohio State University, Columbus, OH; Huimin Chen, <u>J.E. Morral</u>, Department of Metallurgy and Materials Engineering, Institute of Materials Science, University of Connecticut, Storrs, CT.

When two alloys are placed in contact to form a diffusion couple, the microstructure that forms is a function of alloy composition. This function can be illustrated on a phase diagram as an Interdiffusion Microstructure Map (IMM). IMMs can be constructed using computer simulations (e.g. DICTRA), experimental observations, and/or mathematical modeling. For example an IMM was determined for Ni-Cr-Al diffusion couples at 1200°C. The couples consisted of one $\gamma+\gamma'$ alloy bonded to a number of $\gamma+\beta$ alloys. The IMM contained five regions corresponding to five different microstructures. The regions met at a five-line node, giving the map an unexpected topology. It is now believed that IMM's for (γ/β) diffusion couples can have a five line node as well. Ni-Cr-Al diffusion couples of the type $(\gamma/\gamma+\beta)$ have been studied, too. Their IMM contains three regions and a corresponding three-line node where the three regions meet. A general method of anticipating IMM topology using kinetic principles will be discussed.

SESSION E4: PHASE TRANSFORMATIONS IV
Chair: Alan J. Ardell
Monday Afternoon, November 29, 1999
Room 210 (H)

3:30 PM <u>*E4.1</u>
PHASE TRANSFORMATIONS IN MULTILAYER STRUCTURES. <u>Troy W. Barbee, Jr.</u>, Lawrence Livermore National Laboratory, Livermore, CA.

Multilayer structures are a class of kinetically metastable synthetic inorganic solids. Kinetic metastability results from the exceptionally large atomic quench rates characteristic of physical vapor deposition which is the primary synthesis process for these materials. If sample temperatures are low it is possible to fabricate atomic dimension layers (nanometers) of elements which form, under other process conditions, very stable compounds. Additionally, interfacial interactions can determine the structure of individual layers as a result of epitaxial effects or electronic contributions to the interfacial energies. Subsequent thermal processing typically results in the initial formation of metastable interfacially localized reaction products while maintaining the layered structure. Longer time or higher temperature annealing yields the equilibrium phases with subsequent decomposition of the layered structure. In this presentation reactions in the multilayer systems Cu/Zr, Al/Monel 400 (Ni_7Cu_3), Al/Zr and Cu/Cr,Mo,W,Ta,Re will be presented and discussed as characteristic examples of phase transform-ations in multilayer structures. Particular emphasis will be placed on the fundamental information available from quantitative experiments studying phase transformations in multilayer structures.

This work was performed under the auspices of the U. S. Department of Energy by Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48.

4:00 PM *E4.2
GROWTH OF LAMELLAR PRODUCTS DURING DISCONTINUOUS SOLID STATE REACTIONS. Pawel Zieba, Institute of Metallurgy and Materials Science, Polish Academy of Sciences, Cracow, POLAND; Wolfgang Gust, Universität Stuttgart, Institut für Metallkunde, Stuttgart, GERMANY.

The discontinuous solid state reactions represent a group of solid state phase transformations during which the formation of a new phase occurs at a migrating reaction front being a path of rapid diffusion. The discontinuous precipitation (DP) reaction results in the formation of a peculiar lamellar structure of solute-rich β phase and solute-depleted α solid solution. However, the equilibrium state is not reached in the transformation products which is manifested by the presence of a solute concentration profile across the α lamella. The subsequent discontinuous coarsening (DC) reaction, observed after prolonged ageing, removes the excess of the solute atoms and brings the system nearer to the equilibrium state. On the other hand, annealing of the DP products close to the solvus temperature results in a recession of the reaction front of the former DP cell accompanied by the formation of an inhomogeneous $\alpha \sim$ solid solution manifested by a so-called "ghost image" of the previous positions of the β lamellae at which the maximum value of the solute content is expected. In the present paper, the morphology and chemistry of the DP, DC and DD reactions will be discussed mostly based on recent results obtained using analytical electron microscopy and *insitu* observation.

4:30 PM E4.3
FORMATION AND EVOLUTION OF THREE DIMENSIONAL STRUCTURES IN THE Cu/Sn/Si(111) SYSTEM. Qin Hu, I.V. Mitchell, M. Zinke-Allmang, The University of Western Ontario, Department of Physics and Astronomy, London, Ontario, CANADA.

Copper is a prevalent contaminant in silicon device fabrication. Since Cu has a good solubility in Sn, Cu-Sn alloys may be formed to prevent Cu from diffusing into Si substrates. Several Cu/Sn/Si(111) samples were prepared in our molecular-beam epitaxy (MBE) system. By using AFM and SEM, surface structures have been imaged. AES and EDX were used to investigate the composition of differently shaped clusters after annealing. Etching with dilute HCl solutions was used to distinguish the chemical origin of various surface morphologies. The results will be compared with those Sn/Si and Cu/Si samples and a model for the evolution of 3-D structures in this system will be presented.

4:45 PM E4.4
EARLY STAGES OF DECOMPOSITION IN Ni-RICH Ni-Ti. Michael Kompatscher, Helge Heinrich, Jean-Marc Schneider, Bernd Schönfeld, Gernot Kostorz, ETH Zürich, SWITZERLAND.

The decomposition of Ni-rich Ni-Ti involves the formation of two distinguishable $L1_2$-related coherent metastable states [1,2], before the stable η phase (DO_{24}) appears at sufficiently high temperatures. In-situ small-angle neutron scattering was performed on polycrystals and single crystals at temperatures between 900 and 1240 K. The integrated intensity as a function of aging time for polycrystalline Ni-11.3 at.% Ti at 900 K indicates a first plateau that may be related to the γ^{II} state [2]; a Ti concentration of 15.0(3) at.% in the particles and 8.3(3) at.% in the matrix is estimated, fully compatible with the results at 850 K [1,2] and the metastable miscibility gap suggested by Hashimoto and Tsujimoto [3]. The scattering patterns of a Ni-12 at.%

Ti single crystal aged at 1200 and 1240 K showed strong scattering intensities along <001> (related to the coherent γ^{II}/γ^{I} states) and sharp streaks along <111> (related to platelets of the stable η phase). At 1240 K, $L1_2$-related intensities along <001> are unexpected, as the initial state of the alloy is not within the suggested metastable miscibility gap. The results are discussed in the light of available thermodynamical data and diffuse scattering results for the Ni-Ti system.

[1] A. Cerri, B. Schönfeld and G. Kostorz, Phys. Rev. B 42, 958 (1990).
[2] P. Vyskocil, J. Skov Pedersen, G. Kostorz and B. Schönfeld, Acta Mater. 45, 3311 (1997).
[3] K. Hashimoto and T. Tsujimoto, Trans. JIM 19, 77 (1978).

SESSION E5: POSTER SESSION
Chairs: Raul A. Enrique and Celeste Sagui
Monday Evening, November 29, 1999
8:00 P.M.
Exhibition Hall D (H)

E5.1
ADVANCES IN PHASE FIELD APPROACH FOR MICROSTUCTURAL EVOLUTION: INCORPORATION OF RIGID-BODY MOTION AND MOBILITY AND ENERGY ANISOTROPY OF GRAIN BOUNDARIES. Andrei Kazaryan, The Ohio State Univ., Dept. of Physics, Columbus, OH; Yunzhi Wang, Suliman A. Dragia The Ohio State Univ., Dept. of Materials Science and Engineering, Columbus, OH; Bruce R. Patton, The Ohio State Univ., Dept. of Physics, Columbus, OH.

Recent advances in Phase Field modeling of microstructural evolution will be discussed in the context of incorporation of rigid-body motion of grains and mobility and energy anisotropy of grain boundaries. Simulation results for the evolution of pores at grain boundary with the absence and presence of an externally applied force will be discussed in the light of available analytical and numerical data. In the case of anisotropic grain growth, the interplay between the mobility anisotropy and energy anisotropy of grain boundary is investigated. The morphological and topological evolution of an arbitrary polycrystalline microstructure during anisotropic grain growth will be discussed. Possible applications of the model to a variety of problems which require anisotropic boundary properties will be discussed.

E5.2
HARD PARTICLES IN PHASE SEPARATING BINARY MIXTURES AND BLOCK- COPOLYMER FILMS - SIMULATIONS AND THEORY. Valeriy V. Ginzburg, Gongwen Peng, Feng Qiu, Anna C. Balazs, University of Pittsburgh, Dept. of Chem. and Petroleum Engineering; David Jasnow, University of Pittsburgh, Dept. of Physics and Astronomy, Pittsburgh, PA.

We study the influence of hard mobile "filler" particles on the phase separation in binary mixtures and block-copolymer films. By combining the cell-dynamical systems (CDS) equations for the mixture with Langevin dynamics for the particles, and implementing the "perfect wetting" moving boundary conditions, we simulate the role of the particle density, size and mobility on the phase separation dynamics. It is shown that the coarsening slows down, and the domain size is decreased at the late stage, compared with the no-particle system. We propose a mean-field kinetic model to analytically describe this late-stage behavior and find good qualitative agreement between the theory and the simulations. The obtained results qualitatively agree with recent experimental data on the behavior of nanoparticles in thin films.

E5.3
PHASE EVOLUTION AND TRANSFORMATIONS DURING LONG-TERM CREEP OF TWO-PHASE TITANIUM ALUMINIDES. Fritz Appel, GKSS-Research Centre, Institute for Materials Research, Geesthacht, GERMANY.

Titanium aluminides based on the intermetallic γ(TiAl) and α_2(Ti_3Al) phases are being considered as light weight materials for high temperature applications in advanced energy conversion systems. However, for such applications the material suffers from insufficient creep resistance at the intended service temperature of 700°C. The paper reports an electron microscope study of diffusion controlled mechanism which apparently causes the degradation of the strength properties. Climb has been recognized at the dislocation mismatch structures of lamellar interfaces. The processes lead to significant structural changes involving the formation of extended ledges and recrystallization. The driving forces of these mechanisms probably arise from non-equilibrium phase compositions and significant coherency stresses occuring at the interfaces.

E5.4
DIFFUSION PATHWAY OF INTERFACE REACTIONS IN Ni/SiC.

Zhenfu Dong, John H. Perepezko, Univ of Wisconsin-Madison, WI; Alan S. Edelstein, Naval Research Laboratory, Washington, DC.

Silicon carbide plays a very important role in a large variety of materials, not only serving as a semiconducting material for high temperature, high frequency and high power electronic device applications, but also serving as a strengthening fiber in composite structural materials with metal matrices. For both application areas, the stability of the metal contacts with SiC against interdiffusion reactions is one of the limiting factors that must be addressed in processing and use. In order to achieve a control over the interface reactions, the diffusion pathway as well as the phase stability near the metal/SiC interface needs to be established, especially for the initial stage. In order to examine these kinetic issues, annealing studies were conducted on Ni/SiC as a model, prototype system. A special focus was directed to the initial stage of interface reaction.
A multilayer sample of amorphous SiC (a-SiC) and polycrystalline Ni was prepared by ion-beam sputtering. The modulation wavelength is around 80 nm and with equal thickness of a-SiC and Ni layers. Since the interfacial reaction between crystalline SiC (c-SiC) and Ni may differ from that of the a-SiC/Ni interface, a sandwich-structured sample was prepared. For this sample configuration, the Ni layer is covered by c-SiC at one side and by a-SiC at the other side, so that it is possible to obtain results for these two interfaces under identical heat treatment conditions. By use of XRD, TEM and energy disperse spectroscopy (EDS), information on the structural evolution and composition distribution during heat treatment was obtained. The diffusion of Ni into the SiC layer and Si into the Ni layer appear to take place concurrently during the annealing process, followed by phase formation in a sequence of NiSi and Ni_2Si. However, the morphology of the reacted zone near the a-SiC/Ni and c-SiC/Ni interfaces is completely different. For a-SiC/Ni remarkably planar interfaces are maintained while for c-SiC/Ni an irregular reaction front develops. The observed morphology differences can be related to a precursor interdiffusion reaction and the different (metastable) phase stability between a-SiC/Ni and c-SiC/Ni. Phase stability between Ni and SiC is schematically proposed. The support of ONR (N00014-92-J-1554) is gratefully acknowledged.

E5.5
PHASE TRANSITION AND PATTERN OF SELF-ORGANIZED MICROSTRUCTURES IN PRESENCE OF MOBILE IMPURITIES.

Kristinka Ivanova, Institute of Electronics Bulgarian Academy of Sciences, Sofia, BULGARIA; and Marcel Ausloos, SUPRAS, Institut de Physique B5, Université de Liège, Liege, BELGIUM.

A model for thick film growth starting from a surface and the statistical physics of the microstructure and surface roughness has been studied through simulation. The microstructure is described at the mesoscopic (particle) scale. The model is based on the extended Eden model. This leads to the description of the formation of front facets, competition between faces of different orientations and surface roughening, with an interesting microstructure complexity. A dynamical repulsion effect on the front ≫ with the mobile particles has been investigated numerically. The presence of mobile particles shifts the usual percolation transition for 3D systems from 0.65 corresponding to static hindrances, to the value of 0.8. The particle pushing leads to an aggregation phenomenon which self-organizes the particles near and after the interface.

E5.6
THE INTERACTION OF TERNARY SOLUTE ADDITIONS WITH COHERENT Al/Al_3Sc INTERPHASE BOUNDARIES.

Mark Asta, Sandia National Laboratories, Livermore, CA; R. Benedek and D.N. Seidman, Northwestern University, Evanston, IL; L.H. Yang, Lawrence Livermore National Laboratory, Livermore, CA; R.W. Hyland, Jr., Alcoa Technical Center, Alcoa, PA.

Segregation of alloying additions to interphase boundaries in multiphase microstructures can strongly affect the evolution of precipitate shapes and sizes. In this talk we will present results of a collaborative experimental and theoretical study of the segregation of Mg ternary additions to coherent Al/Al_3Sc interphase boundaries in dilute Al-Sc alloys. Large-scale (100-200 atom), first-principles total energy calculations with pseudopotential methods are being performed in order to study the variation in segregation energies as a function of the position of the impurity atom in the vicinity of Al/Al_3Sc interfaces. We find that these segregation energies vary strongly as a function of position, even changing sign as the impurity atom is moved from a Sc nearest-neighbor to a Sc second-neighor site. Experiments are in progress to determine experimentally segregation employing atom-probe microscopy. This research is supported by the Office of Basic Energy Science, Division of Materials Science, of the U. S. Department of Energy.

E5.7
THREE-DIMENSIONAL SIMULATIONS OF QUENCHED ALLOY SYSTEMS IN THE PRESENCE OF EXTERNAL STRESSES.

Daniel Orlikowski, Celeste Sagui, Department of Physics, NC State University, Raleigh, NC; Andres Somoza, Departamento de Fisica, Universidad de Murcia, Murcia, SPAIN; and Christopher Roland, Department of Physics, NC State University, Raleigh, NC.

Elastic fields are known to profoundly influence the phase separation process of binary alloy systems. Such elastic effects derive from a lattice mismatch between the different atomic species, from inhomogeneities in the elastic constants and/or from externally imposed stresses. We have investigated the effects of the latter on quenched alloy systems through large-scale, three-dimensional simulations of an appropriate phase-field model. Specifically, we focus on the transformations that the external stresses induce in the domain morphology, including modifications of a selection criterion for the shape, orientation and phase of the ordered domains. The effects on external stresses on the coarsening rates, structure factor and distribution functions will all be discussed.

E5.8
MECHANISM OF PHASE SEPARATION IN NEAR-ALPHA TITANIUM-RICH Ti-Al ALLOYS.

Heather Liew, Alfred Cerezo, George Smith, Oxford University, Department of Materials, Parks Road, Oxford, UNITED KINGDOM; Jun-ichi Koike, Department of Materials Science, Tohoku University, Aoba-ku, Sendai, JAPAN.

Titanium-rich Ti-Al alloys based on the primary solid solution possess good high temperature properties. Additional strengthening in these near-alpha alloys is achieved by allowing limited formation of the ordered alpha-two phase. This phase is based on the intermetallic Ti_3Al and has an ordered DO19 structure which is closely related to the hexagonal structure of the parent alpha phase. The decomposition sequence occurring in a binary alloy of nominal composition Ti-15 at% Al consisting of supersaturated alpha has been studied by a combination of techniques. A number of experimental analytical methods, including electron microscopy, atom probe field ion microscopy and neutron diffraction, have been utilised in conjunction with atomistic computer simulations to identify the sequence of events occurring during phase separation. Both experimental and modelling results show that extensive ordering occurs in this system prior to detectable phase separation. The local composition differences show a progressive increase in amplitude with time. These results are indicative of a non-classical phase separation mechanism, falling into the class of conditional spinodal reactions. The relatively slow rate of the reaction in Ti-Al means that it is a good model system for the investigation of this poorly understood phase transformation mechanism. Quantitative results and analysis will be presented, and theory and experiment will be compared.

E5.9
EVOLUTION OF STRESS, PHASE FORMATION AND MICROSTRUCTURE IN TiCu-ALLOY FILMS.

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Using a cantilever beam technique the internal stress of TiCu-alloy films on alumina substrates was measured in situ under UHV-conditions as a function of substrate temperature. The alloy components were evaporated from separate evaporation sources. At substrate temperatures below 300°C stress vs. thickness curves indicate the formation of amorphous alloy films. This interpretation is confirmed by TEM-, TED- as well as XRD-investigations of these films. At substrate temperatures between 300°C and 325°C a new feature develops in the stress vs. thickness curve above 20 nm mean film thickness. A strong tensile stress contribution, which correlates with the substrate temperature, is interpreted to be due to changes in the microstructure. Indeed, XRD-data indicate a well developed film texture which is attributed to the δ-phase of TiCu. Qualitatively similar stress changes are found in this temperature range by varying the film stoichiometry by $\pm$ 10%. A slight Ti-excess gives rise to larger tensile film forces leading simultaneously to a better-developed film texture. An excess of Cu, on the other hand, reduces the film texture and the tensile film forces. At temperatures above about 330°C a more or less statistical sequence of tensile as well as compressive stresses is built up during film deposition. TEM-micrographs reveal a polycrystalline film structure and the alloy formed can be identified as the γ-phase of TiCu. Finally we will present the results of experiments in which different alloy films after deposition were annealed for one hour at 450°C. The magnitude of the stress change and thus change in the film microstructure is strongly related to the deposition conditions (substrate temperature and stoichiometry).

E5.10
EUTECTOID DECOMPOSITION IN THREE Ti-Co ALLOYS.

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The mechanisms of eutectoid decomposition are important because of the widespread use of alloys which exhibit a eutectoid transformation. However, the transformation remains a matter of controversy for a number of reasons. The Ti-Co system is examined in order to test current understanding of eutectoid decomposition. The high temperature beta phase can transform on cooling into several products - alpha plates, a non-lamellar mixture of alpha and Ti_2Co which can be designated 'bainite', lamellar pearlite, spherical pearlite and Ti_2Co allotriomorphs. In this study the high temperature beta phase is decomposed (i) in hypoeutectoid, eutectoid and hypereutectoid alloys, (ii) for a range of undercoolings and (iii) with prior thermo-mechanical treatment. The microstructure and crystallography of the transformation products is characterised variously by optical metallography, SEM, XRD and TEM. The classification of the transformation products is discussed. The ability of the theories of eutectoid decomposition to explain the variety of transformation products is explored. The role of nucleation site, crystallography and thermodynamics in the choice of decomposition products are assessed. In conclusion the formation of the various products is compared and contrasted with the types found in ferrous systems.

E5.11
SOLID SOLUTIONS $(PbI_2)_x$-$(BiI_3)_{1-x}$. Yuri N. Dmitriev, Paul R. Bennett, Leonard J. Cirignano, Tapan K. Gupta, Mikhail Klugerman, Kanai S. Shah, Radiation Monitoring Devices, Watertown, MA.

Layered materials have received a lot of attention not only as materials with unusual physical-chemical properties, but also as very promising for various applications (for instance, optical and radiation detectors, elements of electro-chemical batteries). In solid solution form, combination of different materials inclined to mutual solubility allow the possibility of studying the nature of the solubility mechanism and managing physical-chemical parameters of mixed crystals. Systems $(PBI_2)_x$ - $(BiI_3)_{1-x}$ of two layered semiconductors PbI_2 (E_g = 2.3 eV) and BiI_3 (E_g = 1.7 eV) with various compositions (x = 0, 0.3, 0.33, 0.5, 0.67, 0.7, 0.8, 0.9, 0.95, 0.97, 0.98, 0.99, 1.0) were synthesized and grown both as bulk single crystals (by vertical Bridgman method) and films (by thermal vacuum deposition). Grown composites were tested by different techniques (X-ray diffraction analysis, optical transmission, and I - V measurements). Property versus composition curves were plotted and showed nonlinear behavior of measured parameters . The results of studies of numerous physical properties are compatible with the original assumption that the system consists of a limited series of solid solutions. Response of the compounds to X-ray excitation was also measured and demonstrated the maximum value for compounds with x around 1. The structural model of ordered structures formation in this system, which was based upon local electrical neutrality of unit cells, was worked out. The possibility of the formation of crystal structures as ordered sets of BiI_3 and PbI_2 layers was also checked. This was achieved by using the concept of an average size of structural elements in octahedral positions of closest packing of identical spheres that had been developed before. Some potential applications of $(PbI_2)_x$ - $(BiI_3)_{1-x}$ solid solution are discussed.

E5.12
MICROSTRUCTURAL EVOLUTION DURING DO19 TO O-PHASE TRANSFORMATION IN Ti-Al-Nb SYSTEM. Y.H. Wen, Dept of Materials Science and Engineering, The Pennsylvania State University, University Park, PA; Y.Z. Wang, Dept of Materials Science and Engineering, The Ohio State University, Columbus, OH; L.A. Bendersky, Metallurgy Division, NIST, Gaithersburg, MD; L.Q. Chen, Dept of Materials Science and Engineering, The Pennsylvania State University, University Park, PA.

The microstructural development in two Ti-Al-Nb alloys with different Nb content is investigated through computer simulation of the precipitation processes of a coherent orthorhombic phase (O-phase) from a DO_{19} parent phase. The simulation predictions are validated by the concurrent experimental study. It is found that in the alloy with higher Nb content (12.5 at%), the precipitates have either square or rectanglar shapes and their spatial arrangement forms various interesting patterns. In the alloy with lower Nb content (10.0 at%), the dominant morphology for the precipitate is long band and their mutual arrangement also leads to some unique patterns. The predicted morphological patterns agree well with the experimental observations.

E5.13
RECRYSTALLIZATION AND CRYSTAL GROWTH OF TIN(II) BASED NITRATE FLUORIDES IN ATTEMPTS TO RECRYSTALLIZE FLUORIDE ION CONDUCTORS IN NITRIC ACID CONDITIONS. Anthony Collin, Georges Denes, Gwilherm Kerherve, Marc Le Rouzes, M. Cecilia Madamba and Alena Peroutka,

Concordia University, Dept of Chemistry and Biochemistry, Laboratory of Solid State Chemistry and Mossbauer Spectroscopy, and Laboratories for Inorganic Materials, Montreal, Quebec, CANADA.

It is known that some tin(II) containing fluoride ion conductors can be recrystallized from their mother solution right after precipitation. This works particularly well for alpha-$PbSnF_4$, the highest performance fluoride ion conductor. In this work, we have tried to extend the applications of this method by applying it to samples that had already been filtered, washed, and allowed to dry. The dry solid was suspended in water, which was then heated to 90C. Then, small aliquots of concentrated nitric acid were added to the hot suspension until the solid was completely dissolved. Recrystallization occurred on cooling. The minimum amount of acid required to dissolve the fluoride was much higher than when recrystallization is performed in the mother solution. In addition, the material that recrystallized vary, depending on the total amount of nitric used. In all cases, the crystals obtained are very thin sheets, much larger than before recrystallization. Results obtained with $PbSnF_4$, Pb_2SnF_6 and $SrSn_2F_6.H_2O$ will be presented.

E5.14
EFFECT OF IRON ON THE SINTERING OF Al_2O_3-MgO-Fe_2O_3 SPINEL. Ubaldo Ortiz Mendez, Oxana V. Kharissova, Facultad de Ingenieria Mecanica y Electrica, Universidad Autonoma de Nuevo Leon, San Nicolas de los Garza, NL, MEXICO.

The influence of Fe on the microstructure of Al_2O_3-MgO-Fe_2O_3 spinels is described. The spinels were produced by heating of the mixture of initial oxides in an electric arc furnace at $1400°C$ during 12 hrs. A ternary diagram for the concentration ranges:Al_2O_3 (5-75 mol.%), MgO (10-80 mol.%), and Fe_2O_3 (5-70 mol.%) summarizes the constitution of these spinels. Amount, composition and weigth ratio of each phase were determined by X-ray powder diffraction. Microstructure of specimens was characterized by scanning electron microscopy and X-ray spectrometry. Distribution, size, morphology of phases and pores were examined. Microhardness and density measurements of spinels complete this study.

E5.15
CRYSTAL GROWTH OF BETA-SILICON CARBIDE SINGLE CRYSTALS FROM SOME TRANSITION-METAL SILICIDE SOLUTIONS. T. Murata, H. Inui, D.R. Johnson* and M. Yamaguchi, Dept. Materials Science & Engineering, Kyoto University, Sakyo-ku, Kyoto, JAPAN; *School of Materials Engineering, Purdue University, West Lafayette, IN.

SiC has attracted considerable interest as a high-temperature, high-power, and high-frequency semiconductor because of its wide energy band gap, high breakdown electric field and high saturated drift velocity. Beta(3C)-SiC is believed to be superior to Alpha-SiC in terms of saturated drift velocity due to the higher crystal symmetry. Beta-SiC is usually formed in thin-film forms by sublimation and chemical vapor deposition methods, since SiC undergoes sublimation without melting at ambient pressures. Recently, we found that when SiC was melted together with transition-metal disilicides such as $CoSi_2$, $CrSi_2$ and $MoSi_2$, they formed either eutectic or peritectic reactions and that SiC solidified as the primary phase at compositions richer in SiC with respect to the corresponding eutectic or peritectic points. Transmission electron microscopy has indicated that SiC solidified as the primary phase is mostly of the beta-type with being relatively free from defects such as stacking faults and twins. Lattice constants of these beta-SiC does not depend on transition-metal used when determined by convergent-beam electron diffraction (CBED). These are indicative of high-quality of beta-SiC formed in solutions of these transition-metal silicides. We have thus tried to grow beta-SiC single crystals of high-quality by a top-seeded solution growth method using a Czochralski furnace with an induction heater and alpha(6H)-SiC single produced by the Acheson method as a seed. Silicide solutions used contain usually several volume fractions of SiC and they are melted in a SiC crucible. The largest size of SiC single crystals so far we obtained by this method is about 200 and 100 micrometers when measured along the a- and c-axes of the seed crystal. We will present the results of investigation on microstructure and electrical properties of grown SiC single crystals.

E5.16
PHASE TRANSFORMATION AND MICROSTRUCTURAL EVOLUTION IN $TiSi_2$ THIN FILMS PRODUCED BY MAGNETRON SPUTTERING. T. Hashimoto, H. Inui and M. Yamaguchi, Dept. Materials Science & Engineering, Kyoto University, Sakyo-ku, Kyoto, JAPAN.

$TiSi_2$ is widely used as gate-electrode and interconnect materials in microelectronics because of its low electrical resistivity and high-temperature stability. When $TiSi_2$ thin films are formed by co-sputtering Ti and Si at room temperature, they are amorphous.

Upon annealing, these films first crystallize into the metastable C49 structure and then transform into the stable C54 structure. Since the C49 phase exhibits a much higher electrical resistivity than the C54 phase, it is important from an engineering point of view to reduce the C49-C54 transformation temperature, which is usually reported to be 600-800°C. In the present study, we prepared TiSi$_2$ thin films by co-sputtering Ti and Si on silica glass and investigated microstructural evolution and electrical resistivity of these films upon annealing at temperatures between 100 and 800°C. We also prepared ternary TiSi$_2$ containing either Mo, Nb or Au within a few atomic percents to see how these ternary elements affect the C49-C54 transformation behavior. For binary TiSi$_2$, the as-deposited amorphous film exhibits electrical resistivity of 250 $\mu\Omega$cm. Crystallization into the C49 phase occurs at 200°C and this metastable C49 phase persists until the annealing temperature is increased to 700°C at which the C49-C54 transformation starts to occur. While the electrical resistivity gradually decreases with the increase in annealing temperature between 200 and 600°C, the C49-C54 transformation is characterized by a drastic decrease in electrical resistivity. While C49 grains are heavily faulted with 90°-rotational twins, C54 grains are relatively defect-free. Characteristic defects in C54 grains are growth twins with habit planes parallel to (001) and their twinning elements are described by K$_1$=(110), η_1=[$\bar{1}$10], K$_2$=(010) and η_2=[100]. The additions of ternary elements are found to reduce the C49-C54 transformation temperature by about 50°C for Mo and Nb and by 100°C for Au.

E5.17
SILICON CRYSTAL GROWTH ON A Ni SILICIDE SEEDING LAYER BY DC MAGNETRON SPUTTERING. <u>Elena Guliants</u>, Wayne A. Anderson, SUNY at Buffalo, Dept of Electrical Engineering, Buffalo, NY.

DC Magnetron sputtering has been applied to polycrystalline Si growth and yielded a uniform Si film at a deposition temperature below the glass softening point. The approach involves the deposition of a thin Ni film over SiO$_2$ prior to Si sputtering. The interaction of the free electrons of Ni with the covalent Si bonds allows the formation of Ni silicide at the Ni-Si interface immediately after the onset Si deposition. The phase composition of the nickel silicide is controlled by the temperature of deposition and the Si-to-Ni concentration ratio. Thus, at low silicon concentrations, metastable Ni$_2$Si is formed due to its low activation energy of formation. Promptly after that, NiSi forms by consuming more Si provided by the sputter gun. Although NiSi is known to be thermally stable up to 700°C, the deposition temperature of 525-600°C is argued to be high enough for the NiSi transition to the equilibrium NiSi$_2$ due to additional free energy released through the Si crystallization. These Ni silicide precipitates provide the nucleation centers for Si crystal growth. As a result, the polycrystalline silicon film is shown to consist of 0.1-0.5μm grains with preferred (110) orientation without an indication of an amorphous phase. The carrier lifetime of 11μs indicates good electrical properties which makes the film potentially applicable to thin film transistors and solar cells. The Ni prelayer thickness varied in the 5-100nm range is found to appreciably influence the crystal size and preferential crystal orientation. The maximum grain size occurs for a 25nm thick Ni film. Several possible mechanisms responsible for the nickel silicide induced grain growth of silicon alongside with the correlation between the Ni silicide and silicon microstructure are discussed.

E5.18
PROCESS AND MECHANISM OF CoSi$_2$/Si SOLID PHASE EPITAXY BY MULTILAYER REACTION. <u>Bing-Zong Li</u>, Xin-Ping Qu, Guo-Ping Ru, Fudan University, Dept of Electronic Engineering, Shanghai, CHINA; Ning Wang, P. Chu, City University of Hong Kong, Dept of Applied Physics, Hong Kong, CHINA.

The hetro-epitaxy of CoSi$_2$ on Si substrate is of interest from both material research and potential device application. Recent years the solid phase epitaxy of CoSi$_2$/Si hetro-structure has achieved significant progress by a new approach with a Ti-interlayer mediated epitaxial growth. In this work a novel multilayer structure of Co/a-Si/Ti/Si(100) together with the Co/Ti/Si(100) are applied to investigate the process and mechanism of the phase evolution and epitaxial growth of CoSi$_2$. AES, XRD, RBS/Channeling, TEM and sheet resistance measurements are used to characterize the interdiffusion and interreaction process, layer and compound transformation, silicide film growth and their epitaxial quality. The experimental results show that an epitaxial CoSi$_2$(100) layer with prominent channeling effect can be grown by a proper annealing procedure of such a Co/a-Si/Ti/Si(100) multilayer. By adding an amorphous Si layer with certain thickness the epitaxial quality of CoSi$_2$ is significantly improved, and the minimum channeling yield can be lowered to about 5.2%. An amorphous metastable phase layer is formed by a solid state amorphization reaction at the initial stage of the multilayer reaction. This layer acts as a diffusion barrier, which controls the atomic interdiffusion of Co, Si and limits the supply of Co atoms. It has a vital effect on the multilayer reaction kinetics, and therefore, the epitaxial growth of CoSi$_2$ on Si. The kinetics of the CoSi$_2$ growth process from Co/a-Si/Ti/Si and other structures are investigated systematically. The activation energy of interdiffusion process for different multilayer structures is determined and compared. The results show that the epitaxial growth and the film crystalline quality of CoSi$_2$ are related to the activation energy.

E5.19
CONTROLLED PHASE FORMATION BY USING A DIFFUSION BARRIER — THE Fe-Si REACTION. C.C. Theron, A. Falepin, S. Degroote, J. Dekoster, <u>A. Vantomme</u>, G. Langouche, Catholic University Leuven, Dept. of Nuclear and Radiation Physics, Leuven, BELGIUM; H.S. de Waal and R. Pretorius, National Accelerator Centre, Van de Graaff Group, Faure, SOUTH AFRICA.

Normally, in a cleanly prepared thin-film diffusion couple, the sequence in which phases appear as a result of thermal annealing follows a specific pattern. In such a case the terms first phase formation, phase formation sequence and final phase have clear meanings. During reactive deposition epitaxy (RDE) it has been shown that the phases can be formed directly, thereby changing the phase formation sequence found in solid phase growth (SPG). The rate at which atoms arrive at the reaction interface is crucial in determining the phase that is formed and in RDE this control is achieved by matching the substrate temperature with the deposition rate. If these ideas are to be applied to SPG, then one way of controlling the rate at which atoms arrive at the reaction interface, is to let them pass through a diffusion barrier. The flux of atoms through this diffusion barrier is determined by both the composition of the diffusion barrier as well as its thickness. A basic study of the direct formation of FeSi$_2$ through an amorphous diffusion barrier has been undertaken. Rutherford backscattering (RBS), Mössbauer spectroscopy and X-ray diffraction (XRD) measurements of this reaction are presented. Fe-V and Fe-Zr diffusion barriers were co-deposited in UHV conditions onto chemically cleaned Si(100) substrates, followed by a layer of Fe. RBS was used to verify the stoichiometry and determine the thickness of the layers. [57]Fe, a Mössbauer isotope, was selectively placed within the samples, since Mössbauer spectroscopy is ideally suited to distinguish between the different stable and metastable Fe-Si phases that may form in these reaction couples. The results are discussed in terms of what is known about the fundamental diffusion processes occurring in the diffusion barrier as well as the role that thermodynamic driving forces play when the supply rate of reactants is limited.

E5.20
ESTIMATION OF THE CRITICAL RADIUS IN THE NUCLEATION PROCESS OF C54 IN C49 TiSi2: ROLE OF THE DIFFERENCE IN DENSITY. <u>Marcella Iannuzzi</u>, Dmitri Migas, Leo Miglio, INFM and Dip. di Scienza dei Materiali, Univ. di Milano-Bicocca, Milano, ITALY; Valeria Meregalli, Max Plank Institute fur Festkorperforschung, Stuttgart, GERMANY; Maria Grazia Grimaldi, Francesco La Via, INFM, CNR-IMETEM and Dip. di Fisica, Univ. di Catania, Catania, ITALY.

Despite the TiSi2 phase transition between the C49 (metastable, kinetically favoured) structure and the C54 (bulk stable, low resistivity) phase has been extensively studied for metallization and local interconnects of Integrated Circuits, the basic properties of the C49 form are still matter of discussion. In particular, the orthorhombic cell sides, i.e. the volume per formula unit, is larger than the one of the C54 phase, but the quantitative estimation seems to exceed any reasonable volume gap between two polymorphic phases. This issue, still non explained in literature, has a very important consequence on the strain field which could be produced during the nucleation process of the C54 phase and in turn on its critical radius. By XRD analysis and ab initio calculations we make a new estimation of the C49 density and we draw a new prediction of the critical radius which could explain the low kinetics of the transformation in the case of narrow lines.

E5.21
CHARACTERIZATION OF EPITAXIAL GROWTH OF COMPLEX NON-STOICHIOMETRIC SEMICONDUCTING RHENIUM "DISILICIDE" FILMS. <u>A. Misra</u>, M. Verdier, T.E. Mitchell, Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM; J.E. Mahan, Colorado State University, Fort Collins, CO.

The Si-deficient, non-stoichiometric "disilicides" of rhenium, ReSi$_{2-x}$, are narrow band gap semiconductors that are potential materials for infrared detectors. Epitaxial films of ReSi$_{2-x}$ on Si offer the potential of developing heterojunction infrared detection devices where the detector element and the signal processing circuitry can be integrated on one Si chip. We have characterized, through transmission electron

microscopy and ion-channeling, the $ReSi_{2-x}$ and $(Re, Mo)Si_{2-x}$ thin films grown by reactive deposition epitaxy on {100} Si. $ReSi_{2-x}$ thin films exhibit a distorted body-centered tetragonal $MoSi_2$-type structure, and excellent epitaxy on {100} Si since the face diagonal of Si unit cell is equal to the c lattice parameter of silicide. A high density of planar defects is observed normal to the c axis in the film and these may correspond to the collapse and shear of the missing Si layers in the Si-deficient "disilicide" film. The stability of these highly defected structures in thin films are examined by vacuum annealing and alloying with Mo. The defect structures in $ReSi_{2-x}$ thin films are compared to the several complex incommensurate and commensurate structures discovered by us in bulk single crystals of $ReSi_{2-x}$. Isolated voids are also observed at the film-substrate interface and are related to the diffusive growth of silicide during reactive deposition epitaxy. The engineering of the defect and interface structures of these complex, non-stoichiometric silicides for optimized optoelectronic properties are discussed.

E5.22
SELECTIVE ALUMINUM CVD ON Si(100) FROM DMAH. Christophe Bisch, Sven Rogge, Thierry Mélin, G.C.A.M. Janssen, Delft University of Technology, Dept. of Applied Physics, DIMES, Delft, THE NETHERLANDS.

We report on the nucleation of Al deposited by CVD from pure DMAH on Si(100) surfaces. Deposition occurs selectively both on bare Si vs. H-terminated Si as well as on H-terminated Si vs. SiO_2. We investigated the influence of pressure on the nucleation and growth at temperatures below 300°C. Selective deposition of large crystals has been reported for a 1 Torr process [Tsubouchi et al. J. Vac. Sci. Technol. A **10**(4), 856]. At low pressure CVD ($< 10^{-6}$mbar), both direct deposition, as well as selective deposition lead to Al nanostructures that do not form a continuous line [Laracuente et al., Appl. Surf. Sci. **107**, 11], [Mitsui et al., J. Appl. Phys. **85**, 522]. We have studied selective CVD in the 10^{-7} - 10^{-4}mbar range. We have grown grains (size ~1nm) which do not form a continuous line from a dose of 12 to 200L (Langmuir) at T=275°C.Metallic and flat nanostructures (size ~ 20x5x5nm) are grown epitaxially on clean Si at T=275°C with a 1200L dose (10^5mbar, 120s). Ten times larger doses, either by increasing the pressure to p=10^{-4}mbar or the time to t=1200s, each lead to 100nm aluminum structures, which coalesce without forming a pinhole free film. With an intermediate dose, structures (size ~60nm) presenting a majority of pyramids are grown on bare Si. Decreasing the temperature to 240°C has no effect on the nucleation. On H-terminated Si patterns in a 30nm SiO_2 layer, lines down to 50nm wide were covered selectively with Al at p=10^{-4}mbar and T=275°C. When these patterns are subjected to a 12000L dose, coalescing structures (~300nm large, 100nm thick) are deposited without forming a flat film.

E5.23
ANNEALING INDUCED MORPHOLOGICAL CHANGES IN ION IMPLANTED POLYCRYSTALLINE SILICON FILMS. Dave Kharas, Alexander H. King, SUNY Stony Brook, Dept. of Materials Science & Engineering, Stony Brook, NY; Nena Golubovic and Glenn Fricano, Standard MEMS Inc., Hauppauge, NY.

Polycrystalline silicon films were grown to a thickness of 0.45mm on (100) silicon wafers, by CVD at 590°C, using silane. The films were then implanted with boron at 80 KeV to doses of 5E15/cm^2 or 1E16/cm^2 and subsequently furnace annealed at 900°C, 1000°C, or 1100°C. Bright field TEM imaging of the film cross sections reveals annealing induced structural changes relative to the as-deposited and as-implanted structures. At an anneal of 900°C the film retains a columnar grain structure similar to the as-deposited films. Samples annealed at 1100°C are fully epitaxially regrown. However, at the intermediate temperature a three-layer film structure develops in the ion implanted films. The bottom layer, nearest the silicon substrate, is composed of fine columnar grains, a middle layer is apparently single crystalline and the top layer exhibits some implantation induced damage and a fine grain structure. The width of the middle layer is larger with the higher implantation dose. We discuss the possible sources of this layered microstructure in this paper.

E5.24
SIMULATION OF OXYGEN PRECIPITATION IN SILICON CRYSTAL GROWTH AND WAFER PROCESSING - A MECHANISM FOR EXPLAINING LOW TEMPERATURE NUCLEATION KINETICS. Zhihong Wang, Talid Sinno, Robert A. Brown, Department of Chemical Engineering, Massachusetts Institute of Technology Cambridge, MA.

A defining feature of silicon crystals grown by the Czochralski (CZ) method is a high ($O(10^{17} cm^{-3})$) concentration of oxygen atoms which are incorporated by dissolution of the quartz crucible during growth. These levels are above the solubility limit at temperatures prevalent during end-stage crystal growth and wafer processing. The resulting oxide precipitation exhibits highly complex nucleation and growth behavior which has been the subject of intense investigation because of its technological importance in silicon microelectronic device fabrication. A particularly challenging feature is the anomalously high nucleation kinetics observed at lower temperatures (below 600 C). We present a mechanism for explaining a possible source for these observations based on a spatially inhomogeneous incorporation of atomic oxygen into a CZ crystal during growth. Here, previously identified microscale variation of the oxygen concentration in the crystal caused by turbulent fluctuations in the mass transfer in the melt cause greatly amplified nucleation rates for oxygen aggregation in the crystal. This mechanism is first demonstrated by considering a simple model of diffusion and nonlinear reaction which can be analyzed in closed form in the limit of high Damkohler number - reaction rate is much greater than diffusion. Amplifications in nucleation rate greater than 100 times that for a uniform monomor concentration are identified. The mechanism is probed further through simulations of oxide precipitation using a full simulation that accounts for transport, reaction and aggregation of self-interstitials, vacancies, and oxygen. Crystal growth simulations are used to provide realistic and self-consistent initial conditions for the wafer annealing simulations. Thermophysical properties that describe the transport and themodynamic properties of point defects and aggregates needed for these simulations are taken from previous studies of point defect dynamics and experimental measurements. The predictions of the enhancment of oxygen precipitate nucleation and growth agree qualitiatively with the simple model and with experimental observations of the anomalously high nucleation rates seen in precipitation experiments.

E5.25
TWO-DIMENSIONAL SIMULATION OF NUCLEATION AND GROWTH OF MICRODEFECT STRUCTURES IN CZOCHRALSKI-GROWN SILICON. Tatsuo Mori, Talid Sinno and Robert A. Brown, Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA.

Single-crystal silicon crystals grown by the Czochralski method show remarkably reproducible patterns of microdefects formed by aggregation of point defects and impurities, especially oxygen. Numerical simulation is reported for analysis of the two-dimensional dynamics of native point defects and their aggregation during the cooling of a crystal grown by the Czochralski method. The simulations are based on continuum models for point defect diffusion and recombination and models for the aggregation of vacancies to form microvoids and self-interstitials to form distinct precipitates. The models for nucleation and growth of these aggregates are based on discrete rate equations for small clusters and Fokker-Planck equations for large ones. A novel hybrid finite-difference/finite-element method is developed for solving the extremely large discretized equation sets (up to 1×10^7 ordinary differential equations) that result in a transient simulation.The simulations predict the formation of clusters of vacancies and self-interstitials and the transition, within the crystal, of regions dominated by these species. Clusters of self-interstitials results in regions characteristic of A- and B-defects and vacancy clusters are predicted in regions characteristic of D-defects and oxygen precipitates. The region at the boundary between these regions defines a neutral zone that corresponds to the Oxidation-Induced Stacking-Fault Ring (OSF-Ring) is identified and characterized as a function of pull rate. The mechanism for the formation of the OSF-Ring is clearly seen by examining the vacancy distribution in this region. Models for the location of the OSF-Ring based solely on point defect dynamics are shown to be accurate.

E5.26
INFLUENCE OF THE ALLOY COMPOSITION ON THE THERMODYNAMIC PARAMETERS OF NUCLEATION AND GROWTH OF $Si_{1-x}Ge_x$. J. Olivares, A. Rodriguez, J. Sangrador, T. Rodriguez, E.T.S.I.T.- U.P.M., Madrid, SPAIN; P. Martin. J. Jimenez, U. Valladolid, Valladolid, SPAIN; C. Ballesteros, E.P.S.-Universidad Carlos III, Madrid, SPAIN; Mario Castro, CC.FF. UCM, Madrid, SPAIN.

Polycrystalline SiGe films obtained by crystallization of amorphous deposited SiGe are of interest for the fabrication of thin film transistors. We present herein a study about the influence that the alloy composition, x, has on the crystallization process. Amorphous $Si_{1-x}Ge_x$ layers (100nm thick)in the $0 < x < 0.4$ range, were deposited by LPCVD on SiO_2. The alloys were crystallized by solid phase crystallization at 550°C. The crystalline fraction was determined by XRD and Raman spectroscopy as a function of the crystallization time. The transient and the characteristic times were obtained, for the different compositions, by fitting the crystalline fraction to the Avrami model. The grain size was determined by plan view TEM. Using these data we studied the influence of x on the self-diffusion activation energy in the amorphous material (E_d), the cluster formation maximum free energy (ΔG^*) and the difference between the

Gibbs free energy of the amorphous and the crystalline phases($\Delta G'$). E_d was found to follow a linear dependence on x, $E_d \sim 0.6x$ eV, evidencing faster self-diffusion for increasing x. $\Delta G'$ decreases with increasing x, for $x < 0.3$, and increases with x for $x > 0.3$, probably due to the free energy of mixing. Finally, ΔG^* slightly increases with x for $x < 0.3$, and decreases very steeply for $x > 0.3$. For $x < 0.3$ the nucleation rate increases very slowly with x, keeping the growth rate nearly constant, which results in a small decrease of the grain size for increasing x. For $x > 0.3$ the nucleation rate grows very steeply with x, and the growth rate increases more slowly, which results in a larger number of grains with a smaller diameter

E5.27
EFFECTS OF Ge ON THE NUCLEATION AND GROWTH OF $Si_{1-x}Ge_x$. Shinya Yamaguchi, Seong-kee Park, Nobuyuki Sugii, Kiyokazu Nakagawa, Masanobu Miyao, Hitachi Ltd, Central Research Lab, Tokyo, JAPAN.

We have studied the nucleation and growth of $Si_{1-x}Ge_x$ ($x = 0 - 0.3$) on SiO_2 by transmission electron microscopy (TEM) and ellipsometric spectroscopy. The incubation time, defined as the time required to begin nucleation, significantly decreases with an increase of x; we found the nucleation rate of $Si_{0.7}Ge_{0.3}$ was nearly one-hundred times higher than that of Si. This result corresponds to the lower activation energy for nucleation of $Si_{0.7}Ge_{0.3}$, 3.88 eV, compared to 4 eV in the case of Si. Substitutional Ge in Si decreases the bond energy (e.g., 3.73 eV for Si-Si, 3.65 eV for Si-Ge, and 3.56 eV for Ge-Ge bonds), and consequently reduces the volume free energy of nuclei. Since the activation energy for nucleation is determined by a trade-off between the volume and the surface free energy of nuclei, the decrease in bond energy is dominant compared to the increase of surface free energy with an increase of the nuclear radius. The crystallization time, defined as the time required to complete the crystallization after the end of the incubation time, also decreases significantly with an increase of x. We found the x-dependence of the crystallization time was similar to that of the incubation time, implying a strong relationship between the crystallization velocity and the bond energy. Crystallinity, like the crystallization time, is reduced with an increase of x: the average area of a single domain of $Si_{0.7}Ge_{0.3}$ is 15×15 nm^2. The diffusion coefficient of Ge in Si is sufficiently small to prevent migration, so any violation of the $Si_{0.7}Ge_{0.3}$ growth front must be caused by another mechanism, such as stress-induced defects.

E5.28
FORMATION OF METASTABLE, EPITAXIAL $Si_{1-x}Ge_x$ LAYERS ON Si BY STRESS-ASSISTED SOLID-PHASE EPITAXIAL GROWTH. Jennifer F. Sage, Michael J. Aziz, Harvard University, Cambridge, MA; William Barvosa-Carter, HRL Laboratories, Malibu CA; Tony E. Haynes, Oak Ridge National Laboratory, Oak Ridge TN.

A critical Ge-concentration limit exists for the incorporation of Ge into Si during solid-phase epitaxial growth (SPEG) of strained $Si_{1-x}Ge_x$ layers on unstrained Si substrates [D.C. Paine *etal.* J. Mater. Res. 5 1023 (1990)]. Below this critical concentration of Ge it is possible to grow defect-free material. For more Ge-rich compositions, however, stacking faults are introduced during crystallization, driven by the increasing strain in the crystal due to the increasing concentrations of Ge. In this work we investigate the stress-dependence of SPEG of ion-implanted $Si_{1-x}Ge_x$ layers. We find that by completing part of the crystallization of the $Si_{1-x}Ge_x$ layer while mechanically applying tensile stress, the concentration of Ge that can be elastically incorporated into Si during SPEG can be increased. Using optical interferometry and cross-sectional TEM, we find that tensile stress has two principal effects: it reduces interface roughness as growth proceeds, and also inhibits the formation of stacking faults. We discuss our results in relation to current non-equilibrium kinetic and equilibrium thermodynamic theories of interface roughening and defect generation during growth of strained layers.

E5.29
GROWTH OF EPITAXIAL Cu/TiN/6H-SiC(0001) HETEROSTRUCTURES BY PULSED LASER DEPOSITION. A. Kvit, A.K. Sharma and J. Narayan.

Epitaxial Cu/TiN heterostructures were grown on hexagonal (6H)-SiC(0001) substrate by pulsed laser deposition using the domain epitaxy, where integral multiple of lattice constant and major planes match across the interface [1]. Such layers are needed for metallization of SiC bond integrated circuit devices. These Cu and TiN layers on SiC(0001) were grown at 600 degrees C in a high vacuum ($<10^{-6}$ Torr). This structure was characterized using X-ray diffraction technique and transmission electron microscopy. The X-ray diffraction recorded only (111) and (222) reflection of Cu and TiN. The full-width at half maximum of ω-rocking curve of (111) reflection of Cu (0.4 degree) and TEM results indicated a high epitaxial quality. The plan view transmission electron micrograph shows that Cu forms

three-dimensional islands indicating that the Cu/TiN interface energy is very high. The island size varies from 0.2 to 2.5 μm. Analysis of selective aperture diffraction patterns and cross-sectional transmission electron microscopy, including high-resolution imaging, showed relationships Cu(111)//TiN(111)//6H-SiC(0001). The TiN/SiC and Cu/TiN interfaces were locally atomically sharp and free from secondary phases or obvious interdiffusion. Defects in the TiN(111) layers consisted of threading domain boundaries. The mechanism of three-dimension growth of copper on TiN layers was discussed. The electrical characteristics of this epitaxial heterostructure have been studied. [1] J.Narayan et al, Appl.Phys.Lett. 61, 1290 (1992); U.S. Patent 5, 406, 123 (April 11, 1995).

E5.30
Abstract Withdrawn.

E5.31
IN SITU MORPHOLOGICAL STUDY OF THE Al/SiO$_2$ REACTION AROUND THE EUTECTIC POINT. Jean-Philippe Blondeau, Christophe Dumond, Lévy Allam, Laboratoire de Physique Electronique, Université d'Orléans, IUT de Chartres, Chartres, FRANCE; Vincent Fleury, Laoratorie de Physique de la Matière Condensée, Ecole Polytechnique-CNRS, Palaiseau, FRANCE

A lot of attention has been dedicated recently to the morphological aspects of phase transitions. Different systems have been introduced in order to understand the dendrite growth in casting of bulk samples of metals or of model materials. In the context of the electronic industry, thin films of aluminum are deposited on silica substrates. However, the Al/SiO$_2$ interface is not stable, and a chemical reaction leading to oxidation of Al and reduction of SiO$_2$ is observed. It forms spontaneously an Al/Si alloy and Si clusters. This reaction is a limiting factor in high-T tailoring of transistors. We present here, the first *in situ* optical study of the Al/SO$_2$ reaction, in thin films, at temperatures above 500°C. This study reveals an apparent complex diversity of dendritic-like fractal morphologies and spinodal-like patterns as compared to data previously reported. This experiment allows to understand the essential steps of the oxidation of Al by SiO$_2$, and it shows that thermal cycles generate(potentially useful) nucleation centers. More generally, morphological interpretation of out-of-equilibrium growth patterns gives important insight into the coupling between the thermodynamics and the morphological aspects of a thin film chemical reaction. In the case of the Al/SiO$_2$ reaction, quenching and temperature plateaus can be readily related to different pit and cluster morphologies.

E5.32
FORMATION OF SEMICONDUCTOR QUANTUM DOTS IN THIN SiO$_2$ LAYERS BY ION BEAM SYNTHESIS. Johannes von Borany, Bernd Schmidt, Karl-Heinz Heinig and Michail Klimenkov, Forschungszentrum Rossendorf, Institute of Ion Beam Physics and Materials Research, GERMANY; Karl-Heinz Stegemann, and Hans-Jürgen Thees, Zentrum Mikroelektronik Dresden, GERMANY.

The paper reports on the fabrication of semiconductor quantum dots in SiO$_2$ films by ion beam synthesis. Si and/or Ge ions have been implanted with a fluence of about 10^{16}cm^{-2} into thermally grown thin SiO$_2$ layers (d<30 nm) on silicon wafers, which are subsequently annealed. Depending on the implantation and annealing conditions nearly spherical nanoclusters (typical size 3-6 nm) are formed, which are investigated in detail by RBS, STEM-EDX and TEM, respectively. Although the implanted Ge depth profile is distributed over almost the whole SiO$_2$ layer, under specific implantation conditions a very narrow (δ-like) band of nanoclusters close, but well separated from the Si/SiO$_2$ interface can be obtained. The cluster density within this band is in the order of 10^{12}cm^{-2}. The interface band and additional bulk nanoclusters, which may also occur in the SiO$_2$ film are separated by a region without clusters. Theoretical modeling can explain the formation of the interface nanocluster band as a result of ion beam induced collisional mixing and reactions near the Si/SiO$_2$ interface. It will be also shown, that chemical processes, mostly initiated by residual moisture of the annealing atmosphere, influence the cluster evolution and their microstructural state (amorphous or crystalline clusters, oxide clusters). To reduce this influence SiO$_2$/Si$_3$N$_4$ or SiO$_2$/Poly-Si multilayers has been successfully applied. As electrons can be reliably stored even at room temperature in quantum dots the obtained near-interface nanocluster band very well fulfil main requirements for a nanocrystal memory.

E5.33
EFFECT OF IMPURITIES ON THE SIZE AND SHAPE OF CRYSTALLITES AND ON CRYSTAL SYMMETRY: THE CASE OF SUPERIONIC PbSnF$_4$. Georges Denes and M. Cecilia Madamba, Concordia University, Dept of Chemistry and Biochemistry, Laboratory of Solid State Chemistry and Mossbauer Spectroscopy, and Laboratories for Inorganic Materials, Montreal, Quebec, CANADA.

The highest performance fluoride ion conductor, $PbSnF_4$, has been applied for the fabrication of an ambient temperature amperometric oxygen sensor, where it is used in the polycrystalline form. However, the structure of this material is highly anisotropic, thus one could expect polycrystalline samples to give a performance strongly dependent on crystallite direction. This presentation will show that the tin electronic structure has a very strong influence on the local structure, which determines the preferred direction of crystal growth, which is itself responsible for the crystal shape. This, in turn, determines the direction of preferred orientation, which can dramatically alter the properties relative to a randomly oriented sample. The effect of minor impurities on the size of the crystallites and on the crystalline symmetry will be presented.

E5.34
THE PRECIPITATION OF ULTRA-THIN COPPER IN Fe-Cu ALLOYS. <u>Hiroshi Kawanishi</u>, University of Tokyo, Dept of Quantum Eng. and Systems Science, Tokyo, JAPAN; Masahide Suzuki, JAERI, Tokai Establishment, Tokai, Ibaraki, JAPAN.

Ultra-thin copper has been identified by TEM examinations and SADP analysis to be precipitated on the (112) matrix plane in water-quenched Fe-Cu model alloys. Precipitates of this type have the diameter of 20-30 nm and the thickness of less than 0.4 nm, which corresponds to 1-3 atomic layers of (112) copper plane. Copper is shown to be not in solution in the matrix at high temperatures, but to form plate-shaped clusters on (112) iron plane during heat-treatments. In addition to ultra-thin ones, copper platelets (several nm in size) are also formed in specimens though their density is rather low. Both precipitates satisfy a Kurdjumov-Sachs orientation relationship between the matrix and the precipitate. It is pointed out that ultra-thin precipitates are untwinned, whereas platelets are always twinned. Ultra-thin precipitates are confirmed to be mainly responsible for age-hardening by increasing their thickness when specimens are thermally-aged; platelets grow little until specimens show a peak hardness. Ultra-thin precipitates gradually dissolve in the matrix and platelets rapidly grow into disk-shaped precipitates (20-30 nm in diameter) while specimens are over-aged. The strength in the range of over-aging is determined by the evolution of platelets. It is emphasized that the precipitation of ultra-thin copper is similar to the occurrence of GP-zone in for example, aluminum-copper or -silver alloys; the precipitation of ultra-thin copper and GP-zone takes place at the early stage of aging and is replaced by formation of new precipitates with further aging.

E5.35
NANOSCALE TIN INCLUSIONS IN ALUMINUM - STRUCTURE AND MELTING/SOLIDIFICATION PROPERTIES. <u>E. Johnson</u>, C.R.H. Bahl, L. Bendtsen, V.S. Touboltsev, A. Johansen and L. Sarholt, Örsted Laboratory, University of Copenhagen, Copenhagen, DENMARK.

Al-Sn surface alloys with 2-3 at.% Sn have been made by ion implantation of Sn in Al. The microstructure of the alloys consists of dense distributions of nanoscale Sn inclusions embedded in the Al matrix. For implantations carried out at $150°C$ the inclusions have sizes in the range from about 1 to 15 nm. The structure of the inclusions is tetragonal - the white Sn structure - and the lattice parameters are identical to those of bulk tin with a = 0.583 nm and c = 0.318 nm respectively. The inclusions grow in preferred alignment with the matrix and the most commonly observed orientation relationships is given by $(100)_{Sn} \| (111)_{Al}$ and $[010]_{Sn} \| [\bar{2}11]_{Al}$. The shape of the inclusions is partly faceted and partly rounded with larger flat facets on the $(100)_{Sn}/(111)_{Al}$ interfaces. Melting and solidification of the inclusions, which have been studied in-situ by combined TEM and RBS/channeling analysis, shows a distinct hysteresis. Melting of the inclusions is associated with a distinct premelting and takes place in the range from about 160 °C to 210 °C, i.e. significantly below the bulk melting point of 231.9 °C. The premelting is size dependent and the smallest inclusions melt at the lowest temperatures. Solidification requires a substantial undercooling and takes place from around 130 °C, however with a much weaker size dependence.

E5.36
GRAIN GROWTH IN NANOCRYSTALLINE NICKEL AND COBALT ALLOYS. <u>G.D. Hibbard</u>, U. Erb, K.T. Aust, Univ of Toronto, Dept of Metallurgy and Materials Science, Toronto, CANADA; G. Palumbo, Integran Technologies Inc., Toronto, CANADA.

The thermal signal during grain growth of electrodeposited nanocrystalline nickel and cobalt alloys (as-plated grain sizes from $\sim$10 to $\sim$30nm) has been studied via differential scanning calorimetry. The activation energy and the peak temperature of grain growth were used to measure the thermal stability. It has been found that the thermal stability increases with decreasing as-plated grain size. When the total heat released during growth is analyzed in terms of the change in grain boundary area, it is found that the specific grain boundary energy decreases with decreasing as-plated grain size. There are several possible microstructural features that may explain this unusual behaviour, including grain boundary character distribution, solute segregation, texture, and grain size distribution. A series of pre-annealing experiments on as-plated material has been conducted to separate the effects of these variables on the growth behaviour observed with differential scanning calorimetry and transmission electron microscopy.

E5.37
EFFECTS OF BORON DOPING ON THE GRAIN GROWTH BEHAVIOR OF γ/γ' NICKEL-ALUMINUM ALLOY. Y.L. Chiu, <u>A.H.W. Ngan</u>, Dept of Mechanical Engineering, The University of Hong Kong, Hong Kong, P.R. CHINA.

Effects of 0.5 at. % of boron doping on $Ni_{85}Al$ γ/γ' superalloys were investigated for the first time, yielding a number of observations not previously observed in the literature. First, the grain growth kinetics of both the doped and undoped alloys were found to disobey the simple Nielsen law $d = Ct^n$, but instead follow an equation of the type $d = Cln\{t\} + C_0$. The constants C and C_0 were found to be respectively 10.2 and 23.2 for the boron-free alloy, and 6.2 and 14.2 for the boron-doped alloy, i.e., the grain growth rate was retarded significantly upon boron doping. Such a retarding effect is thought to be due to the formation of a boron-nickel cosegregated zone observed at the grain boundaries of the doped alloy; the width of the zone, in μm's, is two to three orders of magnitude larger than the boron induced disordered layer found in nickel rich Ni_3Al compounds doped with boron. Other associated effects of the cosegregated zone include a sharp increase in toughness, much better slip transmission across grains and reduced work-hardening rates. Another intriguing point is that the γ' precipitates were found to segregate to the grain boundaries in the boron-free alloy after cold rolling, but no such segregation of γ' precipitates has been observed in the boron-doped alloy. The different deformation microstructures and the retarded grain growth rates upon boron doping will be discussed, and the possibility of extending the cosegregation induced toughening effects to other intermetallic base systems will be explored.

E5.38
INFLUENCE OF THE ELECTROCHEMICAL ENVIRONMENT ON DIFFUSION PROCESSES NEAR STEP AND ISLAND EDGES: Ag(111). <u>M.I. Haftel</u>, Naval Research Laboratory, Washington, DC and University of Maryland, College Park MD; T.L. Einstein, University of Maryland, College Park, MD.

The electrochemical cell provides a potentially powerful means of altering the morphology and islanding phenomena on metallic surfaces. Diffusion processes near step and island edges, including diffusion over and along step edges, detachment and attachment from step edges, and diffusion around kinks and corners, are known to profoundly affect island sizes and shapes and step morphology. Using the surface-embedded-atom-model (SEAM)[1] for describing metallic surfaces in the electrolytic environment, we calculate the dependence of the activation energies for the aforementioned diffusion processes on the electrochemical potential for the Ag(111) surface. While all these processes show some degree of dependence on the potential, the step-edge barrier and the edge diffusion processes are the most sensitive. Step-edge barriers increase (to over 1 eV) with large positive or negative surface charge, while edge diffusion monotonically decreases with surface charge, varying from 0.15 to 0.50 eV for the range of potentials studied. We discuss what these results imply about electrochemical tuning of island size/shapes and step morphology. *Funding provided by ONR and MRSEC University of Maryland 1. Michael I. Haftel and Mervine Rosen, Phys. Rev. B51, 4426 (1995).

E5.39
AN INVESTIGATION OF TEMPERATURE-MANIPULATED SIZE AND SHAPE EVOLUTION IN SOLUTIONS OF PREFORMED CORE-SHELL NANOPARTICLES. <u>Mathew M. Maye</u>, Wenxia Zheng, Frank L. Leibowitz, Nam. K. Ly, Henry H. Eichelberger, Chuan-Jian Zhong, State University of New York, Binghamton, NY.

Core-shell nanoparticles dissolved in solutions exhibit physical and chemical properties different from their bulk and molecular counterparts that may be manipulated in controllable ways to induce size or shape changes. Based on our recent observation of size and shape evolution of preformed alkanethiolate-encapsulated gold nanoparticles under elevated temperatures (C. J. Zhong, W. X. Zheng, F. L. Leibowitz, Eichelberger, H. H., Chem. Commun., in press), this work investigate further the solution compositions and conditions, and is aimed to understand the fundamental basis of the observed evolution. In addition to remarkable size and shape evolution in which smaller particles evolve towards larger core sizes with well-defined morphology, the evolved nanocrystals also displayed

remarkable propensity of forming long range ordered arrays. While temperature-driven crystal growth is known for non-encapsulated particles on substrate-supported systems, the evolution of the preformed thiolate-encapsulated nanoparticles in solutions into well-defined sizes and shapes represents the first example. Mechanistic aspects involving desorption/re-deposition of the thiolates, coalescence/growth of the cores and solvent composition will be discussed.

E5.40
INTERFACIAL MORPHOLOGY OF ANNEALED Cu-Ag MICROLAMINATES. H.L. Ludtke, G.E. Lucas, Univ of California Santa Barbara, Dept of Chemical Engineering, Santa Barbara, CA; C.G. Levi, Univ of California Santa Barbara, Engineering Materials Dept, Santa Barbara, CA; G.R. Odette, Univ of California Santa Barbara, Dept of Mechanical and Environmental Engineering, Santa Barbara, CA.

Cu-Ag microlaminate composites were fabricated by electron-beam physical vapor deposition to study morphological instabilities. The microlaminates each consisted of five layers, with Cu:Ag layer thicknesses of 2:2, 2:4, 1:4, 4:2 and 4:1 microns. The microlaminates were annealed in an Ar atmosphere for 2, 12, 24, 48 and 192 hours at 900K. Microlaminates were examined after deposition and after heat treatment by scanning and transmission electron microscopy. Increasing time and temperature results in grain growth in both Cu and Ag layers as well as interpenetrations along grain boundaries. The relative length scales of grain size and layer thickness dictate the time to layer breakup.

E5.41
GROWTH STEPS OF (110) DIAMOND USING DICARBON. M. Kaukonen, R.M. Nieminen, Helsinki University of Technology, Helsinki, FINLAND; M. Sternberg, Th. Frauenheim, University of Paderborn, GERMANY.

The growth of nanocrystalline diamond films from C_2 precursors produced by C_{60} fragmentation in hydrogen-poor plasmas has attracted attention because of high growth rates and resulting good mechanical and electronic properties of the films. Since the growth proceeds mainly on the (110) face, we study deposition steps of C_2 molecules onto the clean (110) surface[1] and the lowest-energy configuration of the resulting adsorbate clusters using the density-functional based tight-binding method (DFTB) [2]. Furthermore, we investigate the migration of C_2 molecules near adsorbate clusters by a constrained conjugate gradient method [3] in order to determine energy barriers and diffusion pathways. We find that deposition proceeds by incorporation of C_2 at the ends of C_{2n} zigzag chains along the [100] direction parallel to the surface, either from direct adsorption or after migration along the chains. The diffusion rates of single C_2 molecules on most other parts of the surface is found to be very low due to high barriers. For defect-free growth we find a kinetic energy window for C_2 as the deposition species of $1\ldots2$ eV above kinetic contributions.
[1] P. Redfern et al., *J. Phys. Chem.*, **100** (1996) 11654
[2] M. Elstner et al., *Phys. Rev. B*, **58** (1998) 7260
[3] M. Kaukonen et al., *Phys. Rev. B*, **57** (1998) 9965

E5.42
INTERROGATION OF ALUMINA GRAIN BOUNDARIES BY AFM. P.A. Tibble, B.R. Heywood, Keele University, School of Chemistry and Physics, Keele, UNITED KINGDOM; P. Barnes, R. Richardson, Staffordshire University, Stoke-On-Trent, UNITED KINGDOM.

Since its invention in 1986[1], the Atomic Force Microscope (AFM) has become a powerful tool for the study of surfaces in material science. AFM is capable of imaging surface features from the micron scale right down to the atomic scale without any critical demand for sample preparation. This is particularly advantageous for investigations of ceramic materials where the intrinsic properties are so intimately linked to both their macro and micro-structure. In this paper, we demonstrate the application of AFM to the study of crystalline alumina doped with MgO. Using AFM we have explored the influence of the dopant regime and variuos etching protocols upon microstructural features like pores and cracks, and grain boundaries. Specific measurements of grain-boundary width and depth have been accumulated from a range of samples. When correlated, these data highlight clearly the effect of the heating regime and dwell time upon grain development and, in particular, the role of Ostwald ripening in controlling the evolution of the climax microstructure.
Ref: 1 = Binnig, Gerber, Quate, Physical Review Letters, 1986, 56, p930

E5.43
CRYSTALLIZATION OF TiO_2 IN SOL-GEL DERIVED SiO_2-TiO_2 SYSTEM: FORMATION OF TiO_2 (B) NANOCRYSTALLITES. Toshihiro Kogure, Taku Umezawa, Univ. of Tokyo, Graduate School of Science, Tokyo, JAPAN; Yoshinori Kotani, Atsunori Matsuda, Masahiro Tatsumisago, Tsutomu Minami, Osaka Prefecture Univ, Dept of Applied Material Science, Sakai, JAPAN.

The crystallization of TiO_2 component in monolithic TiO_2 -SiO_2 gels by annealing has been investigated. The crystallization, crystal growth of anatase, and anatase-rutile conversion were gradually suppressed with an increase in the amount of SiO_2 component if TiO_2 /SiO_2 molar ratio is more than 1. TiO_2 (B), one of the polymorphs of TiO_2, were formed as the first crystalline phase by annealing gels with TiO_2 /SiO_2 ratio less then 1 at 800-900°C in air. Transmission electron microscope (TEM) observations revealed that nanocrystallites with a size of 5 -10 nm were dispersed in the amorphous SiO_2 matrix. The X-ray diffraction pattern and lattice fringe spacing in high-resolution TEM images corresponded to those of TiO_2 (B). These TiO_2 (B) nanocrystallites did not grow further but transformed to anatase with a larger crystal size at higher temperatures. TiO_2 (B) nanocrystallites are probably stable with the presence of surrounding SiO_2, presumably with a low interfacial energy, because previous works reported that this phase should be converted to anatase at temperatures around 600°C.

SESSION E6: LIQUID-SOLID TRANSFORMATIONS I
Chair: Heike B. Gabrisch
Tuesday Morning, November 30, 1999
Room 210 (H)

8:30 AM *E6.1
INITIAL CRYSTALLIZATION REACTIONS. J.H. Perepezko, University of Wisconsin-Madison, Dept. Mat. Sci. and Eng., Madison,WI; D.R. Allen, Budd Company Technical Center, Auburn Hills, MI.

During the initial stage of phase formation reactions nucleation conditions often apply a controlling influence on the phase selection, product phase number density and grain size. In most cases the operation of nucleation control is also associated with the development of significant undercooling or supersaturation in order to initiate crystallization. Under this constraint it is common to observe different forms of alloy metastability. In fact, a hierarchy of equilibria can be identified based upon the severity of the kinetic constraints that act during transformation. One consequence of the different levels of metastability is the development of precursor reactions before the initial crystallization. In other cases a kinetic competition between different reaction modes or structures can yield a change in the transformation pathway during reaction. The appearance of kinetic transitions is one consequence of the competition between concurrent reactions and provides a valuable opportunity for kinetics analysis and modeling. In cases where sequential reactions are separated by temperature or time intervals other kinetic constraints operate to expose metastability due to diffusional growth limitations. The identification of the reaction control provides the foundation for kinetics analysis and the development of alloy design strategies. These features can be considered in terms of the observed crystallization behavior during rapid solidification and solid state interface reactions. The support of the ARO (DAAG55-97-1-0261) and ONR (N00014-92-J-1554) is gratefully acknowledged.

9:00 AM *E6.2
MODELING OF SOLID NUCLEATION AND GROWTH IN SUPERCOOLED LIQUID. John P. Leonard and James S. Im, Program in Materials Science and Engineering, Columbia University, New York, NY.

Nucleation and growth of solids in supercooled liquid are encountered in many materials processes. For the case of an elemental system, one can readily identify a parameter dependent growth rate, nucleation rate, and thermal evolution as the fundamental basis of the transformation. A proper and quantitative analysis of the situation, however, is challenging because one must address: 1) Thermal profiles which can be spatially non-uniform and highly transient 2) Rapid interfacial motion that can occur under far from equilibrium conditions and 3) The stochastic nature of nucleation both in time and space.
In this paper, we present a numerical model that incorporates algorithms to simulate nucleation and growth in supercooled liquid in a manner that properly accounts for these above difficulties in a physically consistent manner. The basis of this model relies on a discretization of space and time to address all aspects of the transformation: 1) Heat flow is treated through an alternate-direction explicit finite differences scheme, 2) Interfacial motion is based on

cellular automaton algorithms, 3) Nucleation is modeled as a probabilistic process.

In particular, our formulation of nucleation permits the spatially and temporally random nature of the phenomenon to be manifested in the transformation and resulting microstructure. This is accomplished by calculating the local and instantaneous nucleation probability in each node (based on the temperature, node size, and time step), then comparing it to an instantaneous random number assigned to the node. Nucleation is triggered when this random number exceeds the local and instantaneous nucleation probability. No artificial conditions for nucleation are imposed– allowing nucleation to spontaneously occur based solely on nucleation kinetics. We will demonstrate the effectiveness of the model by analyzing conditions associated with pulsed laser induced crystallization of thin silicon films. This work was supported by DOE under project DE-FG02-94ER45520.

9:30 AM E6.3
MELTING AT THE LIQUIDUS: RAPID MELTING EXPERIMENTS WITH A TITANIUM-NIOBIUM ALLOY. Daniel Josell, William J. Boettinger, Debasis Basak and Sam R. Coriell, National Institute of Standards and Technology, Gaithersburg, MD.

We conducted constant power, pulsed melting experiments using Nb - 47 mass% Ti specimens. Interrupted experiments indicated that the specimen surface and grain boundaries serve as nucleation sites, with the melt fronts moving toward the centers of the grains. The effect the melting behavior of varying the grain diameter and imposed heating rate (just prior to melting) was studied. Simultaneous measurement of the surface radiance temperature and spectral emissivity permitted the specimen temperature to be followed until the specimens, typically > 70% melted, collapsed. Experiments were conducted using specimens with grain diameter between 40 and 167 μm and heating rates from 10^2 to 10^4 K/s. The behavior of the melting specimens recorded in the temperature-time curves differs substantially from that predicted using the equilibrium phase diagram to determine the molten volume fraction as a function of temperature during melting. In order to understand the data, we developed a model of diffusion-limited melting. The model incorporates the spherical grain geometry and imposes solute conservation and local equilibrium at the moving solid/liquid interface. Compositions within the liquid and solid regions satisfy time-dependent diffusion equations as well as boundary conditions at the interface. Thermal diffusion times, much shorter than the time scales of interest, were ignored. In addition to the specimen composition, grain diameter and imposed heating rate, the model uses the ratio of latent heat to specific heat, the liquidus and solidus curves, and the liquid and solid diffusion coefficients. There is good agreement between the melting behavior predicted by the model (with zero free parameters) and the experimental data. In particular, we observed identical melting behavior when the product of heating rate and grain diameter squared was constant, a prediction of the model. No indication of loss of local equilibrium at the solid-liquid interface is implied by the experimental results.

9:45 AM E6.4
NUCLEATION BEHAVIOUR AND SOLID-LIQUID INTERFACIAL ENERGY OF POLYTETRAHEDRAL PHASES. Dirk Holland-Moritz, Institut fuer Raumsimulation, DLR, Koeln, GERMANY and Harvard University, Division of Engineering and Applied Sciences, Cambridge, MA.

According to classical nucleation theory the nucleation- and phase-selection behaviour of undercooled meltallic melts is strongly dependent on the solid-liquid interfacial energy. A structural approach to the modelling of the interfacial energy for simple melt-crystal interfaces (fcc, hcp, bcc) was developed a number of years ago [1,2,3]. In the present work this approach is extended to polytetrahedral phases using numerical simulation. Results of these calculations are presented for different polytetrahedral structures: the tetragonal σ-phase in Ni-V, the monoclinic phase λ-$Al_{13}Fe_4$, the orthorhombic phase μ-Al_5Fe_2 and the icosahedral quasicrystalline I-phase in Al-Pd-Mn. The numerically estimated values for the solid-liquid interfacial energy are compared with results from experiments on the undercooling- and phase- selection behaviour [4]. References: [1] F. Spaepen; Acta Metall. 23 (1975) 729. [2] F. Spaepen and R.B. Meyer; Scripta Met. 10 (1976) 257. [3] C.V. Thompson; Ph.D. Thesis, Harvard University (1979). [4] D. Holland-Moritz; Int. J. Non-Equil. Process. 11, (1998) 169.

SESSION E7: LIQUID-SOLID
TRANSFORMATIONS II
Chair: Ali Chirazi
Tuesday Morning, November 30, 1999
Room 210 (H)

10:30 AM *E7.1
METAL-MEDIATED TRANSFORMATIONS. Robert Sinclair,

Stanford University, Dept of Materials Science and Engineering, Stanford, CA.

It has long been known that some metals (e.g. Al, Ag, Au) bring about the crystallization of amorphous semiconductors at abnormally low temperatures. In situ high-resolution electron microscopy shows that this is a diffusion controlled process, with atomic transport through the metal significantly more rapid than direct rearrangement of the tetrahedral network itself. This metal-mediated-crystallization has been applied to study equivalent phenomenon with respect to amorphous carbon. The reactions become more complex as the metal carbide forming ability increases: nickel and cobalt directly transform the amorphous carbon to graphite, whereas metastable carbides are employed for iron and chromium. No reaction occurs for titanium up to 1000°C. An equivalent reaction appears to take place for the transformation of as deposited beta-tantalum (tetragonal) to the stable BCC phase, employing copper as the mediator. However an amorphous interfacial layer appears integral to the reaction, which has important implications for the use of a tantalum underlayer for copper metallization in integrated circuits.

11:00 AM E7.2
DECOMPOSITION AND CRYSTALLIZATION BEHAVIOR OF Zr AND Pd BASED BULK METALLIC GLASSES. J.F. Löffler, J. Schroers, W.L. Johnson, California Institute of Technology, W.M. Keck Laboratory, Pasadena, CA; W. Wagner, Paul Scherrer Institut, Villigen PSI, SWITZERLAND; P. Thiyagarajan, Argonne National Laboratory, Argonne, IL.

Bulk Metallic Glasses, i.e. multicomponent alloys with a high thermal stability and excellent glass forming ability, can be produced with a diameter of 1 cm or more in their smallest dimension. The best metallic glass formers known so far are $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (Vit1) and $Pd_{40}Cu_{30}Ni_{10}P_{20}$, having critical cooling rates of about 1 K/s and glass transition temperatures T_g of around 636 K and 586 K, respectively, at a heating rate of 10 K/min. We studied the crystallization pathway in both types of alloys by small-angle neutron scattering (SANS), differential scanning calorimetry and scanning electron microscopy. Processing of PdNiCuP in graphite crucibles, using boron oxide flux, enabled us to measure the complete time-temperature-transformation diagram for crystallization in the undercooled melt. These results are compared with earlier crystallization studies on Vit1. Furthermore, we performed *in situ* SANS experiments on both types of alloys at temperatures around T_g. In the *in situ* experiment on Vit1, performed for 15 h at 621 K, an interference maximum developed after 200 min, which increased in intensity and showed a small shift (to lower scattering vectors Q) with increasing annealing time. We conclude that at temperatures near T_g this alloy decomposes on the nanometer scale and forms nanocrystals, as detected by x-ray diffraction, mediated by this decomposition. In contrast, the *in situ* experiment performed on PdNiCuP did not show any intensity change during annealing for 13 h at 571 K, but a drastic change by further annealing at 586 K. At this temperature, the SANS intensity developed spontaneously, with a Q^{-4} dependence in a log-log presentation. This shows that PdNiCuP undergoes a polymorphic transformation rather than crystallization mediated by decomposition, as found in Vit1. In agreement with the SANS data, x-ray diffraction on PdNiCuP, after the annealing at 586 K, showed very narrow Bragg peaks caused by crystals in the micrometer range.

11:15 AM E7.3
TIME DEPENDENT NUCLEATION IN Al-BASED METALLIC GLASSES. T.K. Croat, A.K. Gangpadhyay, K.F. Kelton, Washington Univ, Dept of Physics, St. Louis, MO.

The crystallization kinetics of Al-based metallic glass forming alloys have been analyzed using differential scanning calorimetry and transmission electron microscopy. Multi-step thermal anneals have been applied to crystallize amorphous, rapidly quenched Al-Gd-La-Ni alloys. These techniques yielded further insight into the evolution of nanoscale microstructures common upon devitrification of bulk metallic glasses. Annealed alloys form dense nanoscale crystalline dispersions within an amorphous matrix. Nucleation rates of α-Al grains in the transformed samples were determined directly from microstructural imaging, using transmission electron microscopy. Careful stereological analysis must be employed to obtain statistically valid results. Further data on the transformation kinetics was gathered using isothermal anneals in the differential thermal analyzer. The evidence collected will be used to refine computer simulations based on the classical nucleation theory. Modeling of underlying nucleation phenomena takes into account diffusion through the matrix to the developing cluster as well as attachment rates at the interface. The experimental data allow the dynamical model of the classical theory of nucleation to be evaluated and more realistic models of phase transitions for non-polymorphic systems to be developed. Supported by NASA under contract NAG 5-908.

11:30 AM E7.4
Abstract Withdrawn.

11:45 AM E7.5
Abstract Withdrawn.

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**SESSION E8: LIQUID-SOLID
TRANSFORMATIONS III**
Chair: Susanne Schneider
Tuesday Afternoon, November 30, 1999
Room 210 (H)

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1:30 PM *E8.1
FACETED LIQUID Pb INCLUSIONS IN Al: KINETIC
LIMITATION TO ATTAINING THE EQUILIBRIUM SHAPE.
Heike Gabrisch, Lawrence Berkeley Laboratory, National Center for
Electron Microscopy, Berkeley, CA; Erik Johnson, Anne Vernholt,
Lisbeth Kjelgaard, University of Copenhagen, Örsted Laboratory,
Copenhagen, DENMARK, Uli Dahmen, Lawrence Berkeley
Laboratory, National Center for Electron Microscopy, Berkeley, CA.

Solid Pb precipitates in Al form in parallel orientation with the Al
matrix and take on a cuboctahedral shape. Their aspect ratio c/a of
distances between {100} and {111} facets is a measure of the ratio
between the interfacial energies $\gamma_{\{100\}}/\gamma_{\{111\}}$ between Al and Pb.
During heating above the melting point of Pb the shape of the liquid
inclusions can remain faceted up to 495°C. The degree of faceting is
stronger for larger particles. Using in-situ transmission electron
microscopy, it has been observed that the temperature dependence of
liquid inclusion shapes differs when observed during heating or
cooling, and that the {111} facets exhibit a roughening transition at
495°C. The shape change of the larger liquid inclusions was found to
depend directly on their shape before melting. These observations are
explained in terms of the kinetic limitation to attain equilibrium due
to the necessity to nucleate ledges to advance the {111} interface
when the temperature is below the roughening transition. The model
is also able to explain the size dependence of the observed behavior.
Accurate measurements of particle shapes give the anisotropy of the
interfacial energy between liquid Pb and solid Al. This work is
supported by the Director, Office of Energy Research, Office of
Science, Materials Sciences Division of the U.S. Department of Energy
under Contract No. DE-ACO3-76SFOOO98.

2:00 PM E8.2
A DIFFUSION MONTE CARLO METHOD FOR SIMULATIONS
OF DENDRITIC CRYSTAL GROWTH. Mathis Plapp, Alain Karma,
Northeastern University, Physics Department and Center for
Interdisciplinary Research on Complex Systems, Boston, MA.

The mechanical properties of many commercially important alloys are
considerably influenced by the dendritic microstructures that form
during solidification. A major difficulty for an accurate numerical
modeling of dendrite formation is the difference in length scales
between the details of the growing branched dendrite and the
surrounding diffusion field. We present a novel simulation technique
which is capable of bridging this length scale gap by combining a
diffusion Monte Carlo algorithm and an efficient formulation of the
phase-field method. We use a stochastic representation of the diffusion
field in terms of an ensemble of random walkers, and increase the step
size for the walkers with the distance to the dendrite, to achieve an
efficient integration of the far field. Using this method, we perform
fully quantitative three-dimensional simulations of dendritic growth
under experimentally relevant conditions and find good agreement
with the predictions of microscopic solvability theory. Moreover, we
find that, at low undercooling, the early-stage evolution of the
primary branches is well described by a self-affine scaling, which can
be understood as a diffusion-limited anisotropic Laplacian growth.

2:15 PM E8.3
COUPLING THE NANO AND MICRO SCALES IN MODELING
THE FORMATION OF METALLIC MICRO-STRUCTURES.
A. Chirazi, H. Rafii-tabar, M. Cross, Greenwich Univ, School of
Computing and Mathematical Sciences, London, UNITED
KINGDOM.

The phase transition regime in alloy formation, such as the so called
mushy zone between the liquidus and solidus, plays a significant role
in determining the thermal and mechanical properties of the final
products, as well as the formation of micro-structures. The entire
solidification process is a multi-scale multi-physics process and this
necessitates the explicit inclusion of the nucleation phase of the
atomic clusters in the super saturated liquid state followed by their
dendritic growth into micro-structures within a micro-scale mushy
zone. We have developed a two-level model in which the results on the
nucleation rate and the atomic diffusion parameter obtained at the

nano-scales via Molecular Dynamics (MD) simulations, based on a
many-body inter-atomic potential, is used as input to a generalised
version of the stochastic model of micro-structure formation due
Rappaz et al. The influence of the cooling rate is also included. The
model predicts accurately the formation of inner and outer equiaxed
and columnar zones within the micro-structure and also the creation
of grain boundaries and porosities.

2:30 PM E8.4
FIRST-PRINCIPLES STUDY OF METASTABILITY IN
METAL-BASED SYSTEMS SOLIDIFIED BY DROP-TUBE
PROCESSING. C. Berne, A. Pasturel, B. Vinet, Commissariat à
l'Energie Atomique, Grenoble, FRANCE; M. Sluiter, Institute for
Materials Research, Tohoku University, Sendai, JAPAN.

Under conditions of non-equilibrium thermodynamics, the
solidification of metallic melts may lead to the formation of
metastable crystal structures. The solidification path of highly
undercooled refractory metals and their alloys in a ultrahigh vacuum
drop tube is shown to involve transitory metastable phases. For pure
refractory metals, it may be thought that the high undercooting of a
liquid is favorable to the formation of metastable phases. As such
metastable phases are ephemeral, their characterization is very
difficult. The purpose of this paper is to show how to use
first-principles based total-energy calculations to get some insight into
the physics of the nucleation path. The interplay between local atomic
environment and phase stability properties for tetrahedrally close
packed (tcp) structures in transition metals has been examined using
such calculations. The most probable transitory metastable tcp phases
solidifying from undercooled transition metal melts and the sequence
as a function of composition of tcp phases in the phase diagrams of
many transition metal alloys are shown to have a common origin.
These phenomena are explained in terms of atomic coordination and
level-splitting of the d-like states.

2:45 PM E8.5
OPTIMIZATION OF THE METALLOID CONTENT IN
METAL-METALLOID BULK METALLIC GLASSES. Ou Jin,
Ricardo B. Schwarz, Materials Science and Technology Division, Los
Alamos National Laboratory, Los Alamos, NM.

Bulk metallic glasses are receiving increasing attention for their
potential in applications, and for allowing unprecedented studies of
the structure of liquids and glasses. For conventional metallic glasses
(prepared at cooling rates on the order of 10E6 K/s) it has long been
believed that the metalloid content should be near 20 at.%. Therefore,
the search for new metal-metalloid bulk glass-forming alloys has been
mostly devoted to adjusting the type and content of the metal atoms.
We have studied in detail the effect of phosphorus content on the
formation and properties of bulk metallic glasses in the ternary
Pd-Cu-P and Pd-Ni-P alloy systems. It was found that the bulk glass
forming ability depends sensitively on phosphorus content. Keeping
the Pd/Cu ratio constant, the properties of the Pd-Cu-P glasses as a
function of phosphorus content go through extreme values. For
example, a maximum is observed in the difference between the
crystallization (Tx) and glass-transition (Tg) temperatures, and this
maximum can be used as a simple gauge for optimizing the metalloid
content of the bulk glass. More interestingly, the density as a function
of P content showed a sharp maximum. This maximum correlates
with maxima in Tx-Tg, in the crystallization enthalpy, the bulk
modulus, and with a minimum in the shear modulus. The phosphorus
content at which the properties are extreme depends on the Pd/Cu
ratio. In contrast to these results, the density of Pd-Ni-P bulk glasses
obeys a strict Vegard's law. These results have been applied to the
search of novel ferromagnetic bulk glasses. The presence of maxima in
the properties of Pd-Cu-P bulk glasses is discussed in terms of
short-range order and electronic charge-transfer effects.

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SESSION E9: MARTENSITIC TRANSFORMATIONS
Chair: Pawel Zieba
Tuesday Afternoon, November 30, 1999
Room 210 (H)

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3:15 PM *E9.1
SHOCKWAVE PLASTICITY BY MARTENSITIC-LIKE
TRANSFORMATION MECHANISMS. Brad Lee Holian,
Timothy C. Germann, John P. Hirth, Richard G. Hoagland, and Peter
S. Lomdahl, Los Alamos National Laboratory, Los Alamos, NM;
Ramon Ravelo, Department of Physics, University of Texas at El
Paso, El Paso, TX.

Plastic flow under shock conditions can be accomplished by
mechanisms that closely resemble martensitic phase transformations.
Molecular-dynamics simulations demonstrate that shock waves above
a critical strength, traveling in particular crystallographic directions,

can transform an initial lattice into a compressed matrix interspersed with crystallites of particular orientations. This can be accomplished by uniaxial compression to a coincident-site lattice, followed by shear-plus-shuffle within homogeneous nucleation sites. Relationships of this martensitic-like mode of shock-induced plasticity with true martensitic phase changes will be discussed, including distinct features of dynamic versus static driving conditions.

3:45 PM *E9.2
DIFFUSION CONTROLLED AND MARTENSITIC
TRANSFORMATIONS UNDER THE MICROSCOPE.
Gustaaf Van Tendeloo, Dominique Schryvers, EMAT, University of Antwerp, BELGIUM.

Diffusion controlled as well as non-diffusion controlled transformations can be followed in situ in the electron microscope. Atomic (or nearly) scale images can nowadays be obtained in a temperature range roughly between 5K and 1000K. We will illustrate this for the ordering system Ni-Mo and the martensitic transformation in Ni-Al. In fcc based systems, diffusion controled order-disorder transformations can be followed in the high resolution microscope and with the necessary precautions, the ordering parameter can be measured quantitatively. For Ni-rich Ni-Al material a variety of nucleation and growth phenomena are observed depending on composition and thermal treatment. Rapid cooling produces a martensitic structure with stacking sequences depending on the composition and related with so-called precursor phenomena. Annealing of the B2 phase at $550°C$ produces stable Ni_5Al_3 precipitates growing into plates and formed by a coupling of reordering and displacive reactions. Annealing around $300°C$ forms the metastable w-like Ni_2Al phase by diffusion and shuffling. In Ni-Mn-Ti precipitation of a gamma-brass superstructure is observed yielding dodecahedron shapes bounded by lozenge shaped 110 planes. In more complex systems (such as minerals or ferroelastic materials) the growth of strain minimising variants can lead to the formation of complex domain patterns with specific interfaces.

4:15 PM *E9.3
A STUDY OF PREMONITORY MARTENSITIC SURFACE RELIEF VIA NOVEL X-RAY DIFFUSE AND LASER-LIGHT REFLECTIVITY FROM THE (001) SURFACE OF A $Ni_{63}Al_{37}$ SINGLE CRYSTAL. Uwe Klemradt, Markus Aspelmeyer, Univ of Houston, Physics Dept, Houston, TX, and Univ of Munich, Sektion Physik, Munich, GERMANY; Lowell T. Wood, Simon C. Moss, Univ of Houston, Physics Dept, Houston, TX; Johann S. Peisl, Univ of Munich, Sektion Physik, Munich, GERMANY.

Both x-ray diffuse reflectivity and laser-light scattering have been used to characterize precursor phenomena in the well-known crystal, $Ni_{63}Al_{37}$. The x-ray results show three reversible stages in relief formation with a temperature resolution of less than 1K: 1) enhancement of the Fresnel transmission (Yoneda peak), by more than a factor of three on cooling from 272.5 to 272.0K, 2) reduction of this scattering by more than two orders of magnitude indicating an intermediate faceting transition, 3) suppression of the Yoneda peak due to extensive surface roughening. A novel laser-light scattering method was employed on the same crystal to study time-dependent aspects of the athermal martensitic transformation in which the first observations of an incubation time were found. Using the reflection of a focused HeNe-laser beam, above the conventional M_s, we followed the appearance of macroscopic surface relief as an indicator of the bulk transformation, starting above T_0 where no martensite relief was measured. The reflectivity was continually monitored with a stability of $\pm 0.04K$ and the sample was cooled at 0.1K/sec from 350K to T(hold) above M_s. The incubation time for transformation was the time for a drop in the measured reflectivity. Incubation times above M_s increased from a few seconds at $T(hold)=M_s+0.1K$ by four orders of magnitude at $T(hold)=M_s+0.6K$. Our results conclusively indicate that the athermal start temperature, M_s, occurs when the incubation time for the transformation goes to zero, while above the temperature T_0, the nucleation rate goes to zero. Fits to current theory will be presented. Support for this work came from the Alexander von Humbodlt Foundation (UK), and the NSF on DMR-9729297.

4:45 PM E9.4
NUCLEATION AND GROWTH OF MARTENSITE BY A DEFECT GROWTH. R.C. Pond, Materials Science and Engineering, Department of Engineering, University of Liverpool, Liverpool, UNITED KINGDOM.

The phenomenological theory of martensite crystallography (PTMC) has been extremely valuable in the development of our understanding of these transformations. It provides an algorithm for finding the habit plane where adjacent crystals match, thereby minimising the strain energy associated with the product phase. However, the theory sheds no light on the nucleation and growth mechanism of such transformations. The objective of the present work is to gain greater insight into these processes by exploring nucleation and growth

through interfacial line defects mechanisms which are consistent with the PTMC. The phenomenological and mechanistic models of martensite formation are interlinked because the deformation induced by the motion of a transformation dislocation along an interface and the diffusional flux of material that accompanies such motion are coupled. In particular, it will be shown that diffusionless motion can only arise when the interface is an invariant-plane. Thus, a mechanism which leads to the macroscopically invariant habit plane predicted by the PTMC, must involve growth from a nucleus where the interface remains microscopically invariant at all stages. This requirement limits the crystallographic nature of candidate nuclei to a very small number of possibilities. To illustrate this mechanism the martensitic transformation in NiTi will be discussed. It will be shown how candidate nuclei can be selected, and how the homogeneous strain initially present in a nucleus is relieved by introduction of mobile transformation dislocations (or disconnections) and lattice-invariant twinning. The motion of the disconnections simultaneously causes growth, and the product phase gradually approaches the crystallographic state predicted by the PTMC when the martensite is fully relaxed.

SESSION E10: POSTER SESSION
Chairs: Thomas Kevin Croat and Dirk Holland-Moritz
Tuesday Evening, November 30, 1999
8:00 P.M.
Exhibition Hall D (H)

E10.1
DOMAIN BOUNDARY PRECIPITATION AND DOMAIN GROWTH IN BINARY ALLOYS: MONTE-CARLO SIMULATION. J.-M. Liu, Z.G. Liu, Nanjing University, Laboratory of Solid State Microstructures, Nanjing, P.R. CHINA.

Domain boundary precipitation and domain growth in binary materials are simulated by using the Monte-Carlo method. The simulation is carried out on a hybrid lattice of the spin-exchange Ising model coupled with the Q-state Potts model. The dynamic properties, such as morphology and coarsening kinetics of the second phase precipitates as well as kinetics and scaling of the domain growth, are investigated in details. Pronounced second phase precipitation at domain boundaries is observed. We demonstrate that the domain growth is slowed down due to the precipitates at the boundaries. Both the Lifshitz-Slyozov-Wagner law for second phase coarsening and the linear law for the normal domain growth become broken due to the domain boundary precipitation.

E10.2
EFFECT OF AN APPLIED ELECTRIC FIELD ON THE MORPHOLOGY OF MICROSTRUCTURE OF PERITECTIC ALLOY DURING UNIDIRECTIONAL SOLIDIFICATION. Yuning Jiao, Susumu Takamori, Yoshiaki Ohsawa, Goro Arakane, Akira Sato, National Research Institute for Metals, JAPAN.

A novel experimental method of unidirectional solidification was designed by adding an applied electric field. The experimental results indicated that the influence of electric current density on the morphology and distribution of microstructure of the Cu-85Sn peritectic alloy was very strong. The morphology of the eutectic phase clearly showed the direction of the fluid flow under an applied electric field. With the increasing electric current density, the morphology of the primary phase ϵ was changed from regular plate-like to irregular plate-like and that of the peritectic phase η from dendrite to regular equiaxed grain. An area with a totally peritectic phase could be obtained. The analysis for the experimental results showed that the fluid flow is the main factor which affected the morphology and distribution of the primary and peritectic phase under an applied field.

E10.3
TIME-DEPENDENT NUCLEATION: RECENT ANALYTICAL ADVANCES AND EXPERIMENTAL IMPLICATIONS. Vitaly A. Shneidman, Dept of Materials Science and Engineering, University of Arizona, Tucson, AZ.

In the limit of a high nucleation barrier, $W_* \gg kT$ (k being Boltzmann constant), various forms of the classical nucleation equation (Becker-D, Turnbull-Fisher, Zeldovich-Frenkel) can be solved asymptotically using a matched asymptotic (also, boundary layer) technique. The technique allows one to trace a delicate transition between random nucleation and deterministic growth, and to understand the sensitivity (or, insensitivity) of the results to the selection of a specific nucleation model. The paper reviews the method and recent applications. Those include the effects of a finite rate of a preliminary quench on the transient (isothermal) nucleation kinetics and the effect of pre-existing nuclei; the increase of the Avrami exponent in a typical non-isothermal DTA experiment due to strong time-dependent nucleation effects during rapid quench and

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heating (obtained in collaboration with D. R. Uhlmann), some critical analysis of athermal nucleation, etc.

E10.4
A SELF-SIMILAR SOLUTION FOR THE GROWTH RATE OF A COMPOUND LAYER IN THIN-FILM BINARY DIFFUSION COUPLES. Huifang Zhang, <u>Harris Wong</u>, Louisiana State Univ, Mechanical Engineering Dept, Baton Rouge, LA.

Diffusion controlled growth of a compound phase AnB between two parallel thin films of material A and B is important in electronic materials processing and in synthesis of high-temperature materials using multilayer films. Previous models of the growth rate do not solve the diffusion equation, and thus do not utilize fully the predictive capability. This talk presents a self-similar solution of the diffusion equation with the nonlinear Kirkendall effect included. The nonlinear partial differential equation is converted into a nonlinear ordinary differential equation with a free boundary and solved iteratively by a shooting method. It is found that the intrinsic diffusion coefficients of A and B in AnB are simultaneously determined from the positions of the interfaces without using the concentration profile in the compound phase. An asymptotic analytic solution valid for small differences in the equilibrium interfacial concentrations is obtained and agrees with the numerical results in the appropriate limit. Implications of this complete solution will be discussed.

E10.5
PARTICLE COARSENING IN MULTIPHASE TERNARY SYSTEMS. <u>W.C. Holmes</u>, Taylor Univ, Dept of Physics, Upland, IN; J.J. Hoyt, Sandia National Laboratories, Livermore, CA.

Particle Coarsening in ternary, multiphase – multicomponent, systems is quite different than its binary counterpart in that the presence of one phase can affect the coarsening behavior of another. We have shown by analytic analysis and numerical simulation that the interaction between two coexisting phases depends on: solution thermodynamics, diffusivities, and equilibrium concentration differences between matrix and precipitate phases. Therefore, different ternary systems create different cross phase interactions which affect coarsening behavior. For example, spatial correlations between the two coarsening phases are a strong function of this interaction and can lead to spatial ordering between the two phases. Also, specific ternary systems can produce kinetic instabilities and pattern formation.

E10.6
MICROSTRUCTURE EVALUATION FOR TIME DEPENDENT NUCLEATION PROTOCOLS IN KJMA KINETICS. Eloi Pineda and <u>Daniel Crespo</u>, Dept. de Física Aplicada, Universitat Politècnica de Catalunya, Barcelona, SPAIN.

A populational extension of the KJMA model (PKJMA) which allows to determine the grain size distribution in nucleation and growth kinetics has been developed in the last years. PKJMA is grounded on the mean field hypothesis that the free space around the growing grains is isotropically distributed, independently of the grain radius. Although this approach is perfectly valid for the case of constant nucleation, a detailed analysis of the model shows that this hypothesis does not hold in the case of time dependent nucleation protocols or pre-existing nuclei. In this work the PKJMA model has been improved by estimating the average free surface around the grains as a function of its radius and the time elapsed since nucleation. The resulting model gives quantitative determination of the microstructure developed under a wide variety of nucleation and growth processes. Pre-existing nuclei, constant nucleation, and the combination of both mechanisms are studied. Constant and radius dependent growth rates are also considered. Comparison with Monte Carlo simulations, showing a quantitative agreement, will be presented.

E10.7
3D SIMULATION OF MORPHOLOGY, SPATIAL CORRELATION, AND COARSENING KINEICS OF γ PRECIPITATES IN A Ni-Al ALLOY. <u>Venu Vaithayanathan</u> and L.Q. Chen, Dept of Materials Science and Engineering, Penn State Univ., University Park, PA.

Precipitation of γ' particles from a disordered γ matrix in a $Ni - Al$ alloy is studied. A continuum three-dimensional (3D) phase-field model is employed. The focus is on the evolution of γ' particle morphogy and development of spatial correlations during coherent nucleation, growth and coarsening. The effect of lattice mismatch on the rate of coarsening is investigated. The results are compared with those obtained in two-dimensional simualtions.

E10.8
SIMULATION OF COARSENING KINETICS OF MISFITTING PARTICLES. <u>Andrei V. Nazarov</u>, Mariya G. Ganchenkova, Dept. of Materials Science, Moscow Engineering Physics Institute, Moscow, RUSSIA; and Alexandr A. Mikheev, Dept. of Metal Physics, I.P.

Bardin Central Res. Institute of Ferrous Metallurgy, Moscow, RUSSIA.

We examine how elastic stress, arising from precipitate misfit strains, influences the diffusion fluxes and growth rate of precipitates. The elastic stress influence on diffusion flows in binary alloys is came into account by using new approach. This approach takes into consideration, that the stress fields can alter the surrounding atom configuration and consequently the local magnitude of the activation barrier. The change of activation barrier is obtained to depend on the displacement field, symmetry of crystal and pair potentials of atom interactions. Knowing this change it is possible to calculate the jump rate. The flux expressions are obtained with the help of the hole gas method, by using jump rate. The equation system for two components and vacancies in which the influence of elastic stress on flows are taken into account is resolved in the quasi-stationary approximation. The obtained kinetic equation for the growth rate of a precipitate differs from the corresponding equation of the LS theory. This equation contains the additional terms conditioned by the gradients in both vacancy concentration and misfit strains. The analysis shows that the kinetics of coarsening are altered by these terms, including the possibility of inverse coarsening. Simulation of this process is realized. The temporal dependency of misfitting particle sizes is examined.

E10.9
COUPLED GROWTH IN PERITECTIC ALLOYS. <u>Tak Shing Lo</u>, Alain Karma, Mathis Plapp, Department of Physics, Northeastern University, Boston, MA.

Whether the solidification of peritectic alloys can produce stable coupled growth structures has been a long standing question. Guided by recent experimental observations in the Fe-Ni system, we have carried out a numerical study of directional solidification in this system using the boundary integral method. For low volume fraction of the primary δ-phase, we find that stable coupled growth lamellar structures can exist over a range of wavelength that lies in the negatively sloping part of the undercooling vs wavelength curve, previously thought to be unstable. This stable range decreases as the volume fraction of δ increases. At about 40% volume fraction of δ, and a smaller temperature gradient to interface velocity ratio where the planar δ-liquid interface is morphologically unstable, we find a different kind of structure that consists of cells of δ-phase separated by γ-phase. Interestingly, coupled growth and cellular structures are separated in parameter space by a highly unstable region such that it is not possible to evolve continuously from one type of structure into the other. Our observations are in good overall agreement with experimental results.

E10.10
THE EFFECT OF HEATING RATE ON THE NUCLEATION AND GROWTH OF INTERFACIAL PHASES. <u>David Van Heerden</u>, Kerri J. Blobaum, Andrew J. Gavens, Tim P. Weihs, The Johns Hopkins Univ., Dept of Materials Science and Engineering, Baltimore, MD.

In this paper we examine the effect of very large variations of heating rate ($10^{0°}C$/sec to approximately $10^{6°}C$/sec) on phase sequences and growth morphologies in interfacial reactions in Ni/Al multilayers. The multilayer foils were sputter deposited onto Si wafers, then subsequently peeled from the substrates to obtain free-standing samples. Samples were tested at low heating rates using conventional DSC techniques. The high heating experiments were done by initiating a self-propagating reaction in the foils, then quenching the reaction between two chilled copper plates and examining the quenched front. The phase sequence in the DSC experiments was characterized using XRD, while in the quenching experiments it was characterized using tranmission electron microscopy. We show that the first phase to nucleate at the Ni/Al interfaces is Al_9Ni_2 and its formation is not dependent upon the heating rate. We argue that the formation of this phase is determined by the relative nucleation rates of the various competing phases (Al_3Ni, Al_3Ni_2, etc.) and its morphology is determined by the dominant diffusion mechanism (bulk versus grain boundary) immediately prior to and during its growth. In contrast to the first phase, Al_9Ni_2, the evolution of subsequent phases is dependent on heating rate. At low heating rates the formation of Al_9Ni_2 is followed by Al_3Ni and then the stable phase Al_3Ni_2. In the rapid heating experiments Al_3Ni is absent from this phase sequence as Al_9Ni_2 transforms directly to the stable phase Al_3Ni_2. We will argue that the formation of subsequent phases is mainly determined by the relative growth rates of the competing phases. The results will be discussed in the context of existing theories for nucleation and growth.

E10.11
PHASE FIELD APPROACH FOR COMPUTER SIMULATION OF ANISOTROPIC GRAIN GROWTH. <u>Andrei Kazaryan</u>, Bruce R. Patton, The Ohio State University, Dept. of Physics, Columbus, OH; Yunzhi Wang, Suliman A. Dregia, The Ohio State University, Dept. of

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Materials Science and Engineering, Columbus, OH.

Domain dynamics of a polycrystalline system with both mobility and energy anisotropy of grain boundaries is investigated using the Phase Field Approach. The model incorporates the anisotropy using the Reed-Shockley dislocation model for a two-dimensional square lattice, taking into account both inclination and misorientation properties of the boundary. Kinetics and morphological evolution of the system is characterized as a function of the interplay between the mobility and boundary energy anisotropy. The results show that in the case of a small island grain embedded in a larger grain, the area of the island grain decreases linearly with time independent of both mobility and energy anisotropy. Similar behavior is observed in the case when several grains are embedded in a larger grain. Possible applications of the model to a variety of problems which require anisotropic boundary properties will be discussed.

E10.12
MICRODYNAMIC MECHANISMS OF CRYSTAL GROWTH UNDER APPLIED ELECTRIC FIELDS. Yuning Jiao, Susumu Takamori, Yoshiaki Ohsawa, Goro Arakane, Akira Sato, National Research Institute for Metals, JAPAN.

On the basis of the model of atomic cluster jump theory, a microdynamical model of crystal growth rate was developed under an electric field. The classical continuous growth model seems to be an exception of the new model. Theoretical analysis indicates that the crystal growth rate is dependent not only the nature of the metal, the undercooling and so on, but also the applied electric field. Moreover, a novel model, which shows the effect of an applied electric field on the solute distribution, the constitutional undercooling and the temperature distribution at the solid/liquid interface during unidirectional solidification, has been established theoretically. Analytical results show that the electrotransport of solute strongly influences the solute distribution and then changes the constitutional undercooling and the temperature distribution. But all changes are connected with the electric current direction of the applied electric field (positive or negative). A new critical criterion without the constitutional undercooling in front of the solid/liquid interface is obtained for unidirectional solidification under an applied electric field.

E10.13
OSCILLATORY HETEROEPITAXIAL GROWTH MODES ON THE GROWING TEMPERATURE. Kenji Umezawa, Shigemitsu Nakanisi, Osaka Prefecture Univ, Dept of Materials Sciences, Osaka, JAPAN; Walter M. Gibson, The Univ at Albany, SUNY, Albany, NY.

The growth mode of multi-layers of Au atoms on Ni(111) and Ag on Cu(111) have been investigated over a wide temperature range fromm 170 through 680 K by using time of flight type impact collision ion beam scattering spectroscopy (ICISS). The ICISS spectra were taken by chopping the primary 2 keV-20Ne+ beams and measuring the $180°$ backward scatter of particles. While Au and Ag atoms form (111) epitaxial layers, twins[$\bar{1}\bar{1}2$] and [$11\bar{2}$] planes were present on these fcc metal substrates. Moreover, the relative amount of epitaxed twins show an observed oscillatory dependence on the growing temperature during deposition. It is unusual hetero epitaxial growth behavior results which would have never observed in previous studies.

E10.14
EFFECT OF PRESSURE ON THE KINETICS OF THE $Cd_{21}Ni_5$ INTERMETALLIC GROWTH. L. N. Paritskaya, V.V. Bogdanov, Department of Crystal Physics, Kharkov State University, UKRAINE; Yu S. Kaganovskii, The Jack and Pearl Resnick Institute of Advanced Technology, Department of Physics, Bar-Ilan University, ISRAEL; W. Lojokowski, J. Jun, and A. Presz, High Pressure Research Center, Warsaw, POLAND.

The effect of high isostastatic pressure on the kinetics of growth of the $Cd_{21}Ni_5$ intermetallic phase in two-layer Cd-Ni samples has been studied at temperatures of 473 K and 553 K. Arrhenius equations for both interdiffusion through the growing phase layer and the interfacial reaction have been obtained for the two pressures. The activation volumes have been found to be 0.9V for interdiffusion and 1.6V for interfacial reaction, where V is the average volume per atom in the $Cd_{21}Ni_5$ lattice. Atomistic mechanisms of intermetallic growth are discussed. For the first time the activation volume for the interfacial reaction during growth of the intermetallic phase and for the reaction diffusion have been determined separately.

E10.15
GROWTH STRESS OF THIN Ti-, Al- and TiAl$_x$-FILMS DEPOSITED UNDER UHV-CONDITIONS AND ITS DEPENDENCE ON SUBSTRATE TEMPERATURE. Stefan Lackner and Reinhard Abermann, Institute of Physical Chemistry, University of Innsbruck, AUSTRIA.

The growth stress of metal films was measured continuously both during as well as after their deposition under UHV-conditions with a cantilever beam technique. The metal films were deposited onto 10nm thick alumina substrate films prepared by reactive evaporation of Al in an oxygen atmosphere. The substrate temperature was varied from $\sim 17°C$ to $400°C$. The growth stress of Ti-films indicates a transition from layer to layer growth at low temperature to island growth at substrate temperatures above room temperature due to an increased adatom mobility. It will be demonstrated that the temperature range in which this transition in the growth mode occurs is strongly affected by impurities in the Ti-evaporation source material and gas ambient during deposition. The growth stress of Al-films deposited at room temperature is typical for this low melting point material and is characteristic for island growth. The film stress built up in these films decreases with increasing substrate temperature, while the film roughness increases. In the last part of this paper we will present results of experiments in which the above metals were evaporated simultaneously from separate sources to form TiAl$_x$-alloy films. The results of these experiments show that the growth stress of the alloy films is strongly dependent on alloy-stoichiometry and substrate temperature. Typical results for TiAl$_3$ will be presented. On the basis of our model for the origin of film stress the differences in the growth stress of the various films can be discussed in terms of the film microstructure. The structure deduced from the stress curves is compared with that seen in SEM and TEM.

E10.16
NUCLEATION AND GROWTH PROCESSES IN THE ADSORPTION OF LAYER OF LAYER-BY-LAYER FILMS. Maria Raposo, Universidade Nova de Lisboa, Faculdade de Ciências e Tecnologia, Departamento de Física, Monte Caparica, PORTUGAL; Nara C. De Souza and Osvaldo N. Oliveira Jr., Universidade de Sao Paulo, Instituto de Física de Sao Carlos, Sao Carlos, SP, BRAZIL.

The buildup of a layer of the conjugated polymer poly(o-methoxyaniline) (POMA) onto POMA and poly(vinylsulfonic acid) (PVS) (POMA/PVS) layer-by-layer films was performed. The kinetics of adsorption of POMA is associated with a nucleation process followed by a diffusion controlled growth explained by a Johnson-Mehl-Avrami function with n=1.5. The nucleation process corresponds to a rapid adsorption of the polymer molecules that are near the substrate surface and the initial POMA adsorbed amount is proportional to the POMA concentration solution. The diffusion controlled growth is associated with the last POMA molecules that arrive to the surface and need to overcome the double layer at the interface. This double-layer appears due to the adsorption of a polyelectrolyte that is in contact with the solution. Because the POMA adsorbed amount depends on the molecular weight, experiments have been carried out with POMA samples of distinct molecular weight obtained by precipitation. The effects from polydispersity will also be discussed.

E10.17
GROWTH, MICROSTRUCTURE AND MICRO-RAMAN STUDIES OF RF MAGNETRON SPUTTER DEPOSITED $SrBi_2TaNbO_9$ AND $SrBi_2Ta_2O_9$ THIN FILMS. Srinvas Sathiraju and Ram S. Katiyar, Department of Physics, University of Puerto Rico, San Juan, PR.

There has been an increased interest in Bismuth layered ferro-electric compounds such as $SrBi_2Nb_2O_9$ (SBN), $SrBi_2Ta_2O_9$(SBT) and $SrBi_2Ta_{0.8}Nb_{1.2}O_9$ (SBTN) due to their fatuigue free nature on Pt electrodes. In this paper, we report a systematic study on the growth, microstructure and Micro-Raman studies of radio frequency (RF) magnetron sputter deposited SBT and SBTN films. C-axis oriented and polycrystalline films were deposited on Si and MgO substrates using 2 inch dia stoichiometry targets of SBT and SBTN. Films were characterized using X-ray diffraction (XRD), X-ray photo emission spectroscopy (XPS), Atomic force microscopy (AFM) and micro-Raman spectroscopy. XPS studies of as-deposited SBT and SBTN thin films reveals that the oxygen ions at the octahedra site (BO_6 where B= Ta/Nb) were much more stronger than those at Bi_2O_2 layers. To confirm these observations, we performed post annealing of the as deposited films in oxygen, or nitrogen ambient. A More detailed study on post annealing effects is in progress. Room Temperature micro-Raman studies reveals that the soft modes shifted towards lower frequencies which suggests that the grains are under stress. Temperature dependence (70-580K) micro-Raman studies of SBT and SBTN films, suggests that, the Raman half-width bands in these films discussed in terms of an harmonic processes involving three phonons. However, the main contribution to line broadening appears due to the presence of defects such as oxygen vacancies. A detailed study on the XPS and micro-Raman studies of SBTN and SBT thin films will be presented.

E10.18
EPITAXY OF Pd THIN FILMS ON (100) STRONTIUM

TITANATE: A TWO STEP GROWTH MODEL. Thomas Wagner, Gunther Richter, Manfred Ruhle, Max-Planck-Institut fuer Metallforschung, Stuttgart, GERMANY.

The Pd/SrTiO$_3$ system was used as a model system to study the influence of post deposition annealing on film orientation of MBE grown films. Films which were grown at 700°C displayed the island growth mode and covered the substrate only partially, even at nominal thicknesses well above 100 nm. The Pd islands were oriented epitaxially: (100)SrTiO$_3$ || (100)Pd, [010]SrTiO$_3$ || [010]Pd. In order to grow thin continuous Pd films with epitaxial orientation, a two step growth process was employed: In a first step, 20 nm thin films were grown keeping the substrate at room temperature. These films were polycrystalline and covered the substrate completely. In a second step, the films were annealed at 700°C in UHV. Abnormal grain growth transformed the polycrystalline films into epitaxial films. This method can be used for growing thin epitaxial metal buffer layers with low defect density. Abnormal grain growth transformed the polycrystalline films into epitaxial films. This method can be used for growing thin epitaxial metal buffer layers with low defect density.

E10.19
IN SITU SPECTROSCOPIC ELLIPSOMETRY STUDY OF THE DIAMOND NUCLEATION AND FILM EVOLUTION PROCESSES. G. Morell, University of Puerto Rico, Dept. of Physical Sciences, Rio Piedras, PR; O.L. Figueroa, University of Puerto Rico, Dept. of Physics, Rio Piedras, PR; L.M. Cancel, Pennsylvania State University, Dept. of Chemical Engineering, State College, PA; B.R. Weiner, University of Puerto Rico, Dept. of Chemistry, Rio Piedras, PR.

We have employed in situ spectroscopic ellipsometry in the monitoring and characterization of diamond film growth in a chemical vapor deposition (CVD) system. These measurements were complemented with ex situ characterizations including Raman, XRD and SEM. The diamond deposition process was split into fifteen-minute intervals and the films removed for characterization. This allowed the characterization of the diamond film evolution in the early nucleation stage, the particle growth stage, and the film thickening stage. The ellipsometric measurements were found to be especially useful in the characterization of the transition from scattered nuclei to film. We also found that the temporal behavior of the effective dielectric function of the film can be employed in the real-time characterization of the effects of variations in deposition conditions over film quality and composition. We also monitor the removal of silicon oxide from the silicon surface in real time in order to determine the most appropriate time to admit methane into the system and start diamond growth, and the true substrate surface temperature.

E10.20
Ni-Al FORMATION REACTIONS: CHARACTERIZING THE METASTABLE Al$_9$Ni$_2$ PHASE. Kerri J. Blobaum, Andrew J. Gavens, David Van Heerden, Tim P. Weihs, The Johns Hopkins Univ., Dept. of Materials Science & Eng., Baltimore, MD.

The sequence of phase formation in solid state reactions (SSRs) of Ni and Al has been the subject of much controversy over the last decade. The first phase to form in SSRs, for example, has been reported to be AlNi, Al$_3$Ni, or Al$_9$Ni$_2$, depending on the sample and annealing conditions. One reason for the difficulty in predicting and identifying the first phase is the lack of knowledge about the metastable phase Al$_9$Ni$_2$. While the structure of Al$_9$Ni$_2$ was determined in detail within the last year, the kinetics of its growth and the energy of its formation have not yet been quantified. Here, for the first time, we present enthalpies and activation energies for the formation of Al$_9$Ni$_2$ in Ni/Al multilayers. The Ni/Al multilayers were sputter-deposited with five different bilayer thicknesses and overall thicknesses near 20 microns. Free-standing specimens of these samples were heated in a differential scanning calorimeter (DSC) to 725 C at various rates. The resulting exotherms were analyzed to yield enthalpies and activation energies of formation for Al$_9$Ni$_2$. The subsequent sequence of phases was identified by quenching the reaction in the DSC and characterizing the intermediate products with X-ray diffraction and TEM.

E10.21
THE EFFECTS OF NUCLEATION IN THE TWO STEP GROWTH OF HVPE GaN. Philip R. Tavernier, Edward V. Etzkorn, Yongbo Wang, David R. Clarke, Univ of California Santa Barbara, Materials Dept, Santa Barbara, CA.

The repeatable growth of high quality thick layers of GaN by hydride vapor phase epitaxy generally requires buffer layers or other surface pretreatments to produce morphologically smooth films useful for further device growth. Of the two critical conditions for high quality GaN growth, low impurity content and proper film nucelation, the latter condition inevitably contributes more to the overall growth of high quality films and thus the exclusion of impurities. We have studied a two step growth mechanism which incorporates a low temperature HVPE grown nucleation layer in order to provide a repeatable method of growing GaN with a regularly stepped surface indicative of two dimensional step flow growth. Growth of the nucleation layer, subsequent annealing at high temperatures, and surface pretreatments, have been studied using x-ray diffraction, atomic force, optical, transmission electron, and scanning electron microscopy, in order to establish optimal conditions for this thin low temperature layer. A comparison to nucleation layers grown by metal organic vapor phase epitaxy reveals that similar low temperature layers can be deposited despite a vast difference in the growth kinetics of MOCVD and HVPE. Additionally we have observed macroscopic step bunching during growth and attribute this to the initial conditions of the low temperature nucleation layer prior to growth at high temperatures.

E10.22
GROWTH AND CHARACTERISATION OF GaInSb THIN FILMS. P. Barman, N.P. Singh and Bal Krishan, Department of Physics, Sant Longowal Institute of Engg. & Tech. Longowal, Sangrur, INDIA.

Growth of bulk GaInSb was carried out using high purity metals in microprocessor controlled high temperature furnace. For growing these crystals of various compositions Vertical Bridgman Method was employed. These bulk crystals with various compositions were used as a source material for thin film growth using thermal evaporation method under a vaccuum of the order 10^{-5}torr. The substrates used were high purity quartz glasses. FTIR spectroscopy was carried out for determining the band gap of the film. It is observed that as the Ga composition increases the band gap also increases proportionally.This confirms that the film follows Vegards Law with composition. Other electrical and optical characterisation of the grown film is being carried out and the results will be presented.

E10.23
KINETICS OF β-Si$_3$N$_4$ ANISOTROPIC GROWTH. Lingling Wang, Tseng-Ying Tien, University of Michigan, Dept of Materials Science and Engineering, Ann Arbor, MI.

Surface diffusion controlled mechanism is governing the morphology of the growth front on (0001) basal plane of β-Si$_3$N$_4$. Its significant change from convex to concave shape as a crystal width increasing allows some kinetic parameters to be measured. In this paper, the diffusion coefficient along the basal plane can be determined through statistically measuring growth velocity in length direction. Hence, the viscosity of the grain boundary liquid phase with different chemical compositions can be then estimated. From the results of high resolution TEM study of this growth front, the faceted interface has also been found, thus indicating that the driving force plays an important role in the grain growth of β-Si$_3$N$_4$.

E10.24
THICKNESS INDUCED BUCKLING INSTABILITY OF bcc COPPER FILMS. B.M. Ocko, Brookhaven National Laboratory, Upton, NY; M.A. Pfeifer, O. Robach, I.K. Robinson, Univ. of Illinois, Urbana, IL; R.Randler and D.M. Kolb, Univ. of Ulm, Ulm, GERMANY.

The structure of thin Cu films (1-20 ML) grown on single crystal Ag(100) and Au(100) surfaces has been investigated using surface x-ray scattering. Films grown under vacuum and electrochemical deposition methods show similar structural features; a psuedomorphic, bcc-like Cu phase below a critical coverage (~10 ML), a uniaxially modulated structure above 10 ML, and bulk fcc Cu above ~20 ML. The bcc-like structure is consistent with the 12% lattice constant difference between Cu and either Au or Ag. The modulated structure can be described by a staggered, orthorhombic distortion, consistent with the uniaxially buckled phase observed with STM (electrodeposition)[1]. Under electrochemical conditions the modulation length varies from 60 to 72 Å[1] and under vacuum conditions it varies between 60 and 96 Å. The x-ray measurements conclusively show that the entire copper film restructures and that the resulting strain field propagates into the underlying Ag or Au lattice. The transformation which occurs with thickness is similar to the temperature dependent Martensitic transition observed in some bcc metals. [1] B.M. Ocko, I.K Robinson, W. Weinert, R.J. Randler, and D.M. Kolb, Phys. Rev. Lett. (accepted)

E10.25
LATE STAGES OF THE COARSENING OF $\gamma\prime$ PARTICLES IN Ni-Al AND Ni-Al-Mo ALLOYS. H.A. Calderon, J.J. Cruz, L. Calzado, Instituto Politecnico Nacional, Mexico DF, MEXICO; T. Mori, Washington University; C. Kisielowski, C.Y. Wang, National Center for Electron Microscopy, LBNL, Berkeley CA.

The late stages of the coarsening process of γ' particles in single crystals of the alloys Ni-12 at.%Al and Ni-10%Al-5%Mo, has been investigated after a series of single and double aging treatments. Single aging treatments close to the γ-γ' solvus line produce rapid development of particle shape, size and spatial arrangement. Groups of large rectangular particles form after relatively short aging times. Analysis of the coarsening kinetics and the particle size distributions suggest that such groups result from a mechanism of particle migration. The second aging has been performed at lower temperatures i. e. 923 K and a bimodal particle size distribution is created. Special attention is given to the particle groups that develop in the late stages of ripening. They can be interpreted as a result of splitting of large particles or as a consequence of migration. On one hand, the coarsening kinetics are a smooth function of aging time and the particle size distributions show the development of larger particles as the aging time progresses. This suggests that the formation of particle arrangement and their evolution are controlled by migration. In addition, high resolution electron microscopy (HREM) is used to observe the translation order domains of particles in such particle groups. It is found the order domains are different for particles in a given arrangement. This gives direct evidence that particle groups are formed by migration and that splitting of larger particles is not observed. Theoretical consideration regarding the conditions for particle splitting will also be discussed.

E10.26
DEPENDENCE OF GaN GRAIN SIZE AND DENSITY ON GROWTH PRESSURE. <u>D.D. Koleske</u>, A.E. Wickenden, R.L. Henry, M.E. Twigg, J.C. Culbertson and R.J. Gorman, Naval Research Laboratory, Washington, DC.

The control of grain size is of critical importance in the growth of polycrystalline semiconductor materials, because many physical and electronic properties are strongly influenced by film microstructure. We have recently demonstrated improved electrical properties when heteroepitaxial GaN thin films are grown at elevated pressures in a close-spaced showerhead MOVPE reactor [1]. Improvement was observed in the electrical properties for films grown at 150 torr vs. 76 torr. This improvement was shown to be associated with an increase in the GaN grain size as observed by transmission electron microscopy [1]. In this work, we will present data that clearly demonstrates the influence of growth pressure on the size and density distribution of GaN nuclei. As the growth pressure is increased, the GaN grain size increases while the GaN grain density decreases on both bare sapphire surfaces and on thin AlN nucleation layers deposited on sapphire. GaN growth occurs under non-equilibrium conditions, and the observed changes in the grain size and density are strongly related to the rate of GaN decomposition, which has been shown to increase as the reactor pressure is increased above 100 torr in H_2 [2] and mixed NH_3 and H_2 flows. The importance of controlling the initial GaN grain density and grain size will be discussed in relation to improved electrical properties in bulk GaN films grown for microwave power device applications. Sponsored by the Office of Naval Research. [1] A.E. Wickenden, et al., J. Electron. Mat. 28, 299 (1999). [2] D.D. Koleske et al., Appl. Phys. Lett. 73, 2018 (1998).

E10.27
EVOLUTION OF INTERFACES OF THE LIQUID INCLUSIONS MIGRATING THROUGH A CRYSTAL UNDER NON-STATION-ARY THERMAL CONDITIONS. <u>Vladimir Gershanov</u>, Sergey Garmashov, Andrey Minyaev, Irina Nosuleva, Nickita Ivanov, Rostov State Univ, Dept of Physics, Rostov-on-Don, RUSSIA.

In thermodynamic equilibrium, the shape of a liquid inclusion in a single crystal carries the information about the surface energy anisotropy. The disturbance of equilibrium in the system 'crystal-liquid inclusion' caused by the action of a thermal gradient or small (<10 K) temperature oscillations leads to the movement of liquid-solid interfaces and the evolution of the inclusion shape. Analysis of the non-equilibrium shape of inclusions allows doing the conclusions on mechanism and kinetics of interface processes. Besides, a thermal gradient applied to the crystal is known to cause the migration of liquid inclusions (the thermomigration process). The thermomigration of discrete inclusions is of interest as a method of selective doping of semiconductors. The temperature oscillations affect the interface processes intensity significantly. This phenomenon can be used to control the migration velocity, the inclusion shape and the geometry of p-n-structures produced by the thermomigration method. The influence of the temperature oscillations on the cross-sectional shapes of the cylindrical inclusions migrating through a crystal has been analyzed using computer simulation of the thermomigration process. The simulation is based on numerical solving of the two-dimensional diffusion equation with nonlinear non-stationary boundary conditions. It is shown that the shape taken by the inclusion during the thermomigration process under stationary thermal conditions is changed under the action of temperature

oscillations. The extent of the changes depends on the anisotropy of interface kinetics, on the inclusion cross-section, on the value of the thermal gradient, and on relationship between rates of heating and cooling during the temperature oscillation. The results of the simulation are discussed and compared with the experimental data.

E10.28
A NUMERICAL STUDY OF METASTABILITY IN THE LIQUID-SOLID TRANSITION. <u>M.E. Gracheva</u>, J.D. Gunton, Lehigh University, Dept of Physics, Bethlehem, PA; J.M. Rickman, Lehigh University, Dept of Materials Science and Engineering, Bethlehem, PA.

A numerical study of homogeneous nucleation in the liquid-solid transition is carried out for a one component Lennard-Jones system. The free energy is determined as a function of several reaction coordinates, including the degree of crystallinity and lattice symmetry of the solid, respectively. Various metastable states and nucleation pathways are discussed. The results are compared with previous work, including classical nucleation theory, computer simulation and density functional theory.

E10.29
THE SELF- SEEDED GROWTH PROCESS IN III-V SEMICONDUCTORS USING VERTICAL DIRECTIONAL SOLIDIFICATION TECHNIQUE. <u>D.B. Gadkari</u>, Dept of Physics, Mithibai College, Mumbai, INDIA; K.B. Lal, Dept of Physics, University of Mumbai; B.M. Arora, CMP & MS Tata Institute of Fundamental Research Mumbai.

It is rare that self-oriented single crystals will be grown without the seeded growth. The 2-4 micron band has been very active using variety of As/Sb based materials. This interest has beeen driven by advanced materials growth and process technology for III V materials. Tl-based III-V material has been proposed recently FIR application. Certainly, device application requires high quality substrates for higher performance of devices and industrial yield. We have grown binary - InSb, GaSb, and ternary -InTeSb, InTlSb, InGaSb, GaInSb, bulk crystals using vertical directional solidification, VDS- technique. Moreover, we have made intensive effort and performed experiment to optimise furnace temperature profile, ampoule geometry, charge material's stoichiometry, inert atmosphere and growth rate to yield the Sb-based binary, ternary and multinary single crystals with high crystalline perfection becomes increasingly difficult as process from elemental to multinary semiconductors.
Apparently, It is rare that self-seeded and orientation single crystals are obtained through un-seeded growth. But we have used VDS-technique to grow the bulk crystals without seed. Self-seeded and oriented single crystals such as InSb, GaSb and ternary derivatives have been grown by VDS-technique. Growth are also carried for dopped materials. Experimental results and characterisation reveal that the self-seeded and orientated single crystal growth are possible for III-V compounds by controlling boundary layer, interface shape and interface gradient regions. Essentially, the quality and crystallinity of as grown ingots have been determined by XRD, Hall-Van der Pauw method and FTIR transmission.The composition of substrates have been confirmed by EDAX, EPMA and ICP-AES, Single crystal growth and orientation of as grown ingots are confirmed by Philips X'pert diffractometer. The self-seeded and orientation growth of bulk single crystals of III-V semiconductors and controlled interface gradient region by using VDS-technique will be explained detail.

E10.30
RECRYSTALLIZATION OF CdTe. <u>Jaan Hiie</u>, Tallinn Technical Univ, Inst of Materials Technology, Tallinn, ESTONIA.

$CdCl_2$ heat treatment of CdS/CdTe/glass solar cells in air at temperatures 400 450°C is a traditional Cl-doping procedure. There is no liquid phase formation and no recrystallization because the temperatures are lower than $CdCl_2$-CdTe eutectics (505°C). CdTe grains will be coated by oxydation products that decrease the effectiveness of the solar cells.
We propose the results of the low-temperature (400-500°C) isothermal recrystallization of CdTe submicron powders in the presence of liquid phases like $CdCl_2$-CdI_2 and tellurium as solvents of CdTe. The aim of the investigation was to develop a method of liquid phase recrystallization and sintering for the thin layer structures of CdS/CdTe on the glass. By optical microscopy, SEM and RHEED methods the granulometric structure, grain growth kinetics, perfectness of CdTe crystals, their orientation and structure of the solidified flux phase were investigated on the lapped and etched surfaces of the polycrystalline ingots.

E10.31
COMPUTER SIMULATION OF FRONT GEOMETRY INFLUENCE ON KINETIC PARAMETRES OF SOLID STATE REACTION.

Konstantin V. Tomashevitch, Moscow State Univ, Dept of Chemistry, Moscow, RUSSIA; Sergei V. Kalinin, Alexey V. Lukashin, Moscow State Univ, HSMS, Moscow, RUSSIA.

Modelling of reaction front formation and evolution in kinetically heterogeneous environment was performed and the influence of reaction front geometry on kinetic parameters of reaction was investigated. In suggested model homogeneous mixture of active (high probability of reaction) and passive (low probability of reaction) particles interacts with randomly walking gas particles. Total concentration of gas particles was a constant. During the process basic characteristics of reaction front such as fractal dimension, effective front width and total activity were calculated and snap-shots of front were saved. Analysis of front geometry shows that the front becomes steady-state as time goes and do not change own geometry later. The global fractal dimension of front (D_{glob}) is 1,0 but on small distances front has a fractal properties with local fractal dimension (D_{loc}) equal to 1,3. Total activity of surface is strongly depended on concentration of active phase. Velocity factors calculated for each composition at different temperatures smoothly changes from values corresponding active phase to values corresponding passive phase. Following this, activation energy of process can be higher than activation energy for pure phases.

E10.32
MORPHOLOGY CONTROL OF SULFIDE IN Fe-Cr-S ALLOYS DURING SOLIDIFICATION. Katsunari Oikawa, Tamio Ikeshoji, Tohoku National Industrial Institute, Materials Engineering Division, Sendai, JAPAN; Hajime Mitsui, Tohoku Univ., Sendai JAPAN; Kiyohito Ishida, Tohoku Univ., Dept. of Materials Science and Engineering, Sendai, JAPAN.

The morphology of sulfide in Fe-Cr-S alloys at 0.5-18 mass% Cr and 0.05-0.3 mass% S formed during solidification and the modification by additional elements of Zr, Mn, Ti and C have been investigated by means of optical and scanning electron microscopy. And the constitution of sulfide has been determined by means of X-ray analyses. The morphologies of sulfide in the Fe-Cr-S ternary alloy can be classified into three types: (i) plate-like (ii) fine globular and (iii) coarsened globular sulfides. The plate-like sulfide is formed in Fe-(0.5-1)%Cr-0.3%S and that of composition is iron-rich sulfide. The morphology of sulfide is changed into the coarsened globular sulfide as increasing the Cr content. The size of coarsened globular sulfide is more than 5μm. The fine globular sulfide is formed in the Fe-(1-5)%Cr-0.05%S. The size of that is under 1μm. Additions of Zr and Ti in the Fe-1%Cr-0.3%S based alloy change the morphology from plate-like to rod-like, but addition of Mn doesn't change the morphology. The formation of different morphology sulfide is discussed on phase diagram information.

E10.33
RECRYSTALLIZATION OF TIN(II) BASED MATERIALS AND ITS INFLUENCE ON THE PARTICLE SIZE AND PROPERTIES. A. Collin, Georges Denes, Gwilherm Kerherve, Marc Le Rouzes, M. Cecilia Madamba and Alena Peroutka, Concordia University, Dept of Chemistry and Biochemistry, Laboratory of Solid State Chemistry and Mossbauer Spectroscopy, and Laboratories for Inorganic Materials, Montreal, Quebec, CANADA.

The use of recrystallization has several beneficial effects on the purity and the crystallinity of materials. However, in addition to resulting in purer, bigger and better shaped crystals, it can also result in chemical changes by reacting with the solvent. Recrystallization at high temperature can result in metastable phases being formed, or on the other hand, if metastable phases being destabilized on annealing, to give phases stable at a lower temperature. Such phenomena have been observed in attempts to recrystallize tin(II) containing fluoride ion conductors. The production of larger crystals obtained on recrystallization also resulted in substantial changes of some of the materials properties. These effects will be presented and correlated to the local atomic structure, to the crystal structure, and to the spatial correlation of the particles.

E10.34
HOW A FAILURE OF RECRYSTALLIZATION TURNS TO BE AN ADVANTAGE: THE FIRST PREPARATION OF SUPERIONIC BaSnF4 BY THE WET METHOD. Georges Denes and Abdualhafeed Muntasar, Concordia University, Dept of Chemistry and Biochemistry, Laboratory of Solid State Chemistry and Mossbauer Spectroscopy, and Laboratories for Inorganic Materials, Montreal, Quebec, CANADA.

In our search for new tin(II) materials with high performance fluoride ion conductivity, the preparation of materials was carried out from aqueous solutions of tin(II) fluoride and barium chloride. For X>0.20 to 0.33, depending on conditions, where X is the molar fraction of barium chloride in the reaction mixture, i.e. X = BaCl2/[BaCl2 + SnF2], hitherto unknown phases were obtained. At higher X (X>0.71

to 0.83, depending on conditions), a Ba(1-x)Sn(x)Cl(1+y)F(1-y) fully disordered solid solution with the BaClF structure is obtained, i.e. no superstructure reflection and no unit-cell distortion is observed. Therefore Ba and Sn are fully disorderd, and so are yCl and (1-y)F on the F sublattice for y>0, or -yF and (1+y)Cl on the Cl sublattice for y<0. When the material obtained by adding the barium chloride solution to the tin(II) fluoride solution (Ba → Sn), for X = 0.735 to 0.870, is stirred 24 hours in water for purification and recrystallization purposes, leaching of some material accounting for about half the sample mass takes place, and the solid residue is pure high performance fluoride ion conductor BaSnF4. The synthesis of BaSnF4 by the dry method (BaF2 + SnF2 at T>400C under inert conditions) was performed by Denes et al. earlier, however, no synthetic route by the wet method had been established before the present work. The details of the new preparation and the properties of BaSnF4 of wet origin will be shown and compared to BaSnF4 from the dry method.

E10.35
RECRYSTALLIZATION AND GROWTH OF STANNIC OXIDE PARTICLES. Georges Denes, Arnaud Gueune, Eva Laou and Stephane Le Huerou, Concordia University, Dept of Chemistry and Biochemistry, Laboratory of Solid State Chemistry and Mossbauer Spectroscopy, and Laboratories for Inorganic Materials, Montreal, Quebec, CANADA.

We have discovered two novel and unusual methods for preparing very small particles of stannic oxide. Contrary to the literature method, which involves the hydrolysis of tin(IV) salts, our new methods consist in the oxidation of tin(II) fluoride. In our first method, selected amounts of hydrogen peroxide are added to SnF_2 in aqueous solutions. Its results in a precipitate of a fine white powder of hydrated stannic oxide $SnO_2 \cdot 2H_2O$. Under moderate heating, it dehydrates to amorphous SnO_2 without recrystallization, and at higher temperatures, it slowly recrystallizes to cassiterite SnO_2 (rutile type structure). The second method consists in heating solid SnF_2 in air. It was found that crystallites of SnF_2 are naturally coated with a very thin passivating layer of SnO_2, undetected by X-ray diffraction. On heating in air, the layer of SnO_2 becomes thicker and the growth of the SnO_2 crystallites, which was monitored, is determined by the rate of diffusion of O_2/H_2O through the layer. The growth of the SnO_2 particles as a function of heating conditions will be shown.

E10.36
UNUSUAL PHENOMENON OF INTERNAL LATTICE BENDING - A NEW MODE OF CRYSTAL GROWTH IN AMORPHOUS FILMS. Vladimir Yu. Kolosov, Ural State Economic Univ, Engineering Dept, Ekaterinburg, RUSSIA.

Crystallisation of amorphous film carries specific features because of thin-film state, peculiar properties of amorphous phase and its metastable nature. Growth can be accompanied by formation of exotic structures (e.g., inherent in "spherulite" and "explosive" crystallisation). We discovered more general and much more complex microstructures (unusual for solid state physics) developed during amorphous - crystalline transformation [1]. In the present paper the main features of the phenomenon revealed by transmission electron microscopy (using primarily bend-contour technique [1] and in situ studies) for some chalcogenides, oxides and metals are described. Unusual atom ordering (translation and small rotation) results in strong (up to 120° per micron) regular, dislocation independent internal bending of the crystal lattice planes (IBCLP). It corresponds to permanent rotation of the unit cell round axes lying in the film plane at the front of a growing crystal. The geometry and the magnitude of IBCLP depends upon a substance, crystallization conditions, orientation of the crystal nucleus, presence of the sublayers, film thickness and composition. IBCLP demonstrates maximum-containing function against growth rate (in the range 10^{-2}-10^3 μm/s) which in turn may be constant or may vary rhythmically because of the crystal anisotropy. IBCLP is increasing (tenfold) upon decreasing film thickness (100-15nm). Different geometries of IBCLP are described. Dynamic changes of diffraction contrast for the large growth rates (revealed by analysis of the video) fit the proposed mechanism of IBCLP formation based on surface nucleation. Hypothetical atomistic model corresponding to conformal transformation of usual crystal lattice is also proposed. Microstructure with IBCLP can be considered as an intermediate between amorphous and crystalline. Probably it is one of the reasons of easy erasable phase-change optical memory in chalcogenide thin-film systems. 1. Kolosov V. Yu., Proc. XII ICEM, Seattle, San Francisco Press, v.1, 574 (1990). This work is partially supported by RFBR grant 97-02-17784.

E10.37
ON THE EFFECT OF Au ADDITION AND THE ROLE OF ALLOY ELEMENT ON NANOCRYSTALLIZATION OF Fe-Zr-B AMORPHOUS ALLOY. Yuan Zhang, Nelia Wanderka, Ulrich Czubayko, Heinrich Wollenberger, Hahn-Meitner-Institute Berlin

GmbH, GERMANY; Fengwu Zhu, Department of Materials Physics, University of Science and Technology Beijing, CHINA.

Atom probe field ion microscopy (APFIM) and transmission electron microscopy (TEM) were applied to examine the local chemical compositions as well as the microstructures of Fe-7Zr-5B-1Au and Fe-14B amorphous alloys during the processes of primary crystallization in order to understand the role of alloy element and the effect of Au addition on the nanocrystallization of Fe-Zr-B amorphous alloys. Au rich clusters were formed during primary crystallization of Fe-7Zr-5B-1Au alloy. However, no α-Fe particle was observed to be present at the sites of Au clusters, suggesting that Au addition can not increase nucleation density of α-Fe, unlike the case of Cu addition. In the as-melt-spun stage, all alloy elements were homogeneously dissolved in Fe-7Zr-5B-1Au alloy. In the early stage of primary crystallization, Zr and Au were still distributed uniformly in the amorphous matrix, however, heterogeneities of Fe and B were evolved. In Fe-14B alloy, Fe and B atoms were found to distribute heterogeneously even in the as-melt-spun stage. It appears that B is helpful to cause compositional fluctuations of Fe while Zr may have an opposite effect. During primary crystallization, Zr atoms were almost completely rejected from α-Fe in Fe-7Zr-5B-1Au alloy. B was found to be highly supersaturatedly dissolved not only in the nanometer sized α-Fe particles formed in Fe-7Zr-5B-1Au alloy, but also in those with large diameters formed in Fe-14B alloy. It is concluded that Zr effectively controls the growth of α-Fe particles and B would play a role on decreasing the nucleation barrier.

E10.38
SHORT-RANGE ORDER AND NANOCRYSTALLIZATION IN AMORPHOUS $Zr_{54.5}Ti_{7.5}Cu_{20}Ni_8Al_{10}$. <u>L.-Q. Xing</u>, Xiaofeng Gu, T.A. Lusby, A.J. Melmed and T.C. Hufnagel, Johns Hopkins University, Department of Materials Science and Engineering, Baltimore, MD.

The alloy $Zr_{54.5}Ti_{7.5}Cu_{20}Ni_8Al_{10}$ has a critical cooling rate of ~ 10 K/s, low enough to allow formation of a bulk metallic glass. Field ion microscopy images reveal that samples of this metallic glass formed even at very high cooling rates (above 10^5 K/s) have regions of short-range order (SRO) less than a nanometer in diameter. The presence of these clusters after rapid solidification indicates that the thermodynamic driving force for their formation must be quite large, even though the absence of crystals suggests that there is a kinetic barrier to the formation of ordered regions larger than the critical nucleus size for crystallization. By comparing crystallization characteristics of several alloys, we conclude that the SRO clusters have an icosahedral structure. The SRO clusters enhance the nucleation rate of the amorphous alloy, in which the primary precipitates are icosahedral quasicrystals. The Ti content of the alloy has a strong influence on the formation of these icosahedral clusters. In $Zr_{54.5}Ti_{7.5}Cu_{20}Ni_8Al_{10}$ the nucleation rate is high, so that the amorphous alloy transforms to a nanocrystalline structure with grains $< 2 - 3$ nm in diameter. Due to the small grain size, x-ray diffraction patterns from this structure resemble that of an amorphous alloy, but differential scanning calorimetry reveals that the structures are in fact different. We have investigated the nanocrystalline structure by means of field ion microscopy, high resolution transmission electron microscopy, and small-angle x-ray scattering.

E10.39
CRYSTALLIZATION OF $Zr_{41}Ti_{14}Cu_{12}Ni_{10}Be_{23}$ MELTS. <u>Jan Schroers</u>, William L. Johnson, Keck Laboratory of Engineering Materials, California Institute of Technology, Pasadena, CA; Ralf Busch, Department of Mechanical Engineering, Oregon State University, Corvallis, OR.

The crystallization behavior of the bulk glass forming $Zr_{41}Ti_{14}Cu_{12}Ni_{10}Be_{23}$ is investigated. Isothermal undercooling experiments are carried out on samples cooled from the equilibrium melt as well as on amorphous samples heated into the supercooled liquid region. The large stability against crystallization of this alloy enables isothermal crystallization studies at the same temperature on amorphous samples heated and samples cooled from above the liquidus temperature. Additionally, constant heating and cooling experiments are performed. A rate of about 1 K/s is sufficient to suppress crystallization of the melt upon cooling from the equilibrium liquid. Upon heating amorphous samples, in contrast, a rate of about 200 K/s is necessary to avoid crystallization. To study the influence on the crystallization of the conditions by which the amorphous sample is prepared, liquid samples are quenched with different rates into the amorphous state and subsequently heated with a constant rate, where crystallization is investigated. An other method to study the history dependent on the crystallization behavior is to cool the sample with a constant rate to different minimum temperatures and afterwards heat with a constant rate and measure the onset of crystallization. The calculated difference in the cooling and heating rate as well as in the history dependence is discussed within a model

that is based on the assumption that the maximum of the nucleation rate is at lower temperatures than the maximum of the growth rate. Therefore nuclei formed at the maximum of the nucleation rate are exposed to a different growth rate while heating and cooling.

E10.40
CRYSTALLIZATION OF GLASSES: ESTIMATING THE DISTRIBUTION OF QUENCHED-IN CRITICAL CLUSTERS USING MECHANISM–MODE NUCLEATION DIAGRAMS. <u>M.A. Crowder</u> and James S. Im, Prog. in Materials Science and Engineering, Columbia Univ., New York, NY.

It is recognized that the mode and rates of crystallization of a glass can depend on the presence and population of quenched-in crystal clusters that originate during the formation of the glass. As such, an accurate estimation of the population of such clusters is of interest in analyzing the crystallization behavior or determining the stability of the glass.
In this paper, we show that it is possible to extract such information from the mechanism–mode diagram that was developed to convey the thermal and athermal mechanisms and steady-state and transient modes of nucleation [Appl.Phys. Lett. **72** (1998) 662]. Construction of mechanism–mode diagrams requires only those thermodynamic and kinetic quantities that are needed for calculating the steady-state nucleation rates and isothermal induction times. By constructing such mechanism–mode diagrams for lithium disilicate and $Au_{81}Si_{19}$ systems, and comparing the resulting information to those that are obtained via numerical simulations, we show that the use of mechanism–mode diagrams is a convenient means of easily and rapidly assessing the crystal cluster evolution during a quench, from which it is possible to identify the approximate final distribution of crystal clusters and estimate the population of quenched-in clusters. Previously, obtaining such information required extensive simulations of cluster dynamics for each specific quenching condition, or involved analytical treatments that are approximate and limited in applicability. In contrast to these approaches, the mechanism–mode-based analysis provides the relevant information in a manner that is both simple and intuitive for arbitrary quenching conditions.

E10.41
A RAMAN STUDY OF A METASTABLE CRYSTALLINE STATE IN AMORPHOUS SiGe LAYERS UNDER CW LASER ILLUMINATION: INFLUENCE OF THE TEMPERATURE. P. Martin, <u>J. Jimenez</u>, Dept Fisica Materia Condensada, ETSII Univ Valladolid, Valladolid, SPAIN; J. Olivares, A. Rodriguez, T. Rodriguez, Dept Tecnologia Electronica, ETSIT Univ Madrid, Madrid, SPAIN.

Amorphous Si and SiGe are normally crystallized for TFTs by either SPC (Solid Phase Crystallization) or laser melting and solidification. The mechanisms involved in the crystallization are a matter of debate. In particular, laser induced crystallization can be done by means of pulsed or continuous laser beams. It was shown that the crystallization of amorphous materials under cw laser beams depends on the incident laser power density. Full crystallization is done for laser power densities above a threshold value. Below such a thershold the existence of metastable crystalline states have been reported for different amorphous materials. We present herein a study of this effect on amorphous SiGe layers grown by LPCVD (Low Pressure Chemical Vapour Deposition) on SiO_2. The metastable crystallization is monitored by Raman spectroscopy as a function of the temperature. For a given composition of the layer and continuous illumination with an Ar^+ laser (514.5 nm), the characteristic Raman spectrum of crystalline SiGe is observed at a determined temperature threshold. When cycling around such a temperature the Raman spectrum evidences changes in the structure of the SiGe layer, shifting from amorphous to crystalline and viceversa. The existence of this metastable crystalline state is discussed in terms of the alloy composition, the laser power density and the temperature.

E10.42
EVOLUTION OF MICROSTRUCTURE AND TEXTURE IN Ti FILMS DEPOSITED ON AMORPHOUS SiO_2. <u>D.N. Dunn</u> and R. Hull, University of Virginia, Department of Materials Science and Engineering, Charlottesville, VA; F.M. Ross and R.M. Tromp, IBM Research Division, Yorktown Heights, NY.

We investigate the evolution of microstructure and texture in Ti films deposited on amorphous SiO_2 using a novel in-situ ultra high vacuum (UHV) transmission electron microscope. In this instrument, deposition and electron microscopy analysis take place within a single UHV environment, thus the critically perturbing effects of contamination can be avoided. In addition, UHV-TEM offers several advantages over other surface sensitive in-situ techniques because both bulk crystal and surface structure can be investigated at video rates.

In this work, we investigate initial structure, morphology and orientation of Ti films using UHV-TEM. Ti films ranging in thickness from 2.5 nm to 10 nm were deposited in-situ upon amorphous SiO_2 at substrate temperatures ranging from room temperature to 350 °C. These films were then examined using selected area electron diffraction and real time video imaging. At room temperature, even films as thin as 2.5 nm showed a strong preferred orientation. Between 2.5 nm and 5.0 nm however, a sharp transition to a [001] preferred orientation was observed. This preferred orientation persisted in films up to 10 nm in thickness. In contrast, at a substrate temperature of 200 °C, we observed a randomly oriented film. Bright- and dark-field imaging show that these films have a surprisingly similar grain size and shape dependence upon thickness and that they grow by a three-dimensional island mechanism. These data will be discussed in terms of probable heterogeneous nucleation mechanisms and appropriate growth models.

E10.43
GROWTH OF PbS SEMICONDUCTOR NANOCRYSTALLITES IN BOROSILICATES AND PHOSPHATE GLASSES. K. Yukimitu, V.C.S. Reynoso, C.L. Carvalho, J.C.S. Moraes, University of Sao Paulo State-UNESP, Faculty of Engineering/Ilha Solteira, Dept. of Physics and Chemistry, Ilha Solteira, Sao Paulo, BRAZIL; S.R. Teixeira, University of Sao Paulo State-UNESP, Faculty of Science and Technology/Pres. Prudente, Dept. of Physics, Chemistry and Biology, Presidente Prudente, Sao Paulo, BRAZIL.

Semiconductor doped glasses(SDG) have been under intensive study during last years. Their study are related to potential applications of the glasses in non-linear optics and integrated optics. Several glass matrices such as borosilicates, phosphates and others were doped with semiconductors like as: PbS, PbSe, PbTe, CdTe etc. The aim of this work is to compare the growth characteristics of PbS nanocrystallites in SiO_2-ZnO-B_2O_3-Na_2O, SiO_2-ZnO-B_2O_3-K_2 and P_2O_5-Na_2O-ZnO-PbO glass systems. The glasses were synthesized by melting the initial oxides in electric furnace specially designed to produce reducing atmosphere. The melting was quenched between two stainless steel plate. In both cases, borosilicate and phosphate glasses, the as cast glass presented light yellow coloration indicating that doping was realized. The melting temperature for borosilicate was about 1150°C and for phosphate glass 1000°C. The annealing temperature for growth of PbS quantum dots in phosphate glass samples(450°C) was less than annealing temperature of silicate glass samples(530°C). The annealing temperature, higher than Tg temperature, was stablished by differential thermal analysis-DTA-technique. Measurements of absorption spectra of the silicate and phosphate glass samples demonstrated a shift of their absorption edges after annealing and increasing the annealing time increased the shift too. Whereas the annealing time for phosphate glas was several minutes, for silicate several hours was necessary. All of these results will be presented simultaneously with x-ray diffraction data for quantum dots growth kinetic discussion.

E10.44
NUCLEATION IN UNDERCOOLED Co-Pd ALLOYS. D. Holland-Moritz[1,2], Th. Schenk[1] and D.M. Herlach[1]; [1]Institut für Raumsimulation, DLR, Köln, GERMANY; [2]Harvard University, Division of Applied Sciences, Cambridge, MA.

Previous studies have shown that Co-Pd alloys could be undercooled near to their magnetic Curie-temperature [1]. By magnetic measurements the onset of magnetic ordering in liquid state was evidenced [2,3]. The dependence of undercooling on the composition of Co-Pd alloys hint on magnetically induced crystal nucleation in the undercooled melts [4]. In the present work the statistics of crystal nucleation are studied for $Co_{1-x}Pd_x$ alloys with x=0.18, 0.25, 0.3, 0.5. Each alloy in diameter of 5 mm was undercooled more than 100 times applying electromagnetic levitation for containerless undercooling. A model developed by Skripov is utilised to statistically analyse the distribution of maximum undercoolings with respect to the origin of nucleation. The results of these investigations indicate that nucleation is influenced by magnetism when the nucleation temperature is approaching the Curie-temperature. References: [1] D. Platzek, C. Notthoff, D.M. Herlach, G. Jacobs and K. Maier, Appl. Phys. Lett. 65 (1994) 1723. [2] J. Reske, D.M. Herlach, F. Keuser, K. Maier and D. Platzek, Phys. Rev. Lett. 75 (1995) 737 - 739. [3] D. Herlach, C. Bührer, D.M. Herlach, K. Maier, C. Notthoff, D. Platzek and J. Reske, Europhys. Lett. 44 (1998) 98 - 102. [4] D.M. Herlach, D. Holland-Moritz, Th. Schenk, K. Schneider, G. Wilde, O. Boni, J. Fransaer and F. Spaepen, accepted for publication in J. Non-Cryst. Sol.

8:30 AM *E11.1
STOCHASTIC MODELING OF GRAIN GROWTH AND COARSENING. C.S. Pande and R.A. Masumura, Naval Research Laboratory, Washington, DC.

Recent experimental and theoretical developments in the modeling of grain growth and coarsening are briefly reviewed. Common characteristics of both these phenomena are briefly pointed out. A formulation based on stochastic consideration is proposed. This formulation assumes that the rate of growth of an individual grain or a precipitate is not entirely determined by its size but has a random component to it. This leads to a Fokker-Planck Equation for the size distribution. The late stage self-similarity or scaling observed in normal grain growth and coarsening is derived from the evolution of these systems using stochastic considerations. It is shown that there is indeed a unique state (the self-similar state) which is in general reached from an arbitrary initial state. The treatment also disputes the notion of multiple steady states in these systems. The case of two dimensional grain growth is treated in detail as an example. Both the time dependence of average grain size and the grain size distribution are obtained from these considerations and shown to be in good agreement with experiments.

9:00 AM *E11.2
NUCLEATION AND GROWTH OF COHERENT PRECIPITATES AT DISLOCATIONS - A PHASE-FIELD MODEL INTEGRATING DEFECT AND PHASE MICROSTRUCTURES. S.Y. Hu and L.Q. Chen, Dept of Materials Science and Engineering, Penn State Univ, University Park, PA.

A phase-field model for studying the coupling between defect distributions and microstructure evolution is proposed. In particular, examples of nucleation and diffusional growth of coherent precipitates at static edge dislocations will be presented. It is shown that nucleation and growth of coherent preciptiates may become barrierless outside a coherent spinodal line as a result of elastic interactions between the dislocations and solid solutions. The effect of a dislocation and elastic anisotropy on the precipitate shape and morphology during nucleation and growth will be discussed. The work is supported by the NSF.

9:30 AM E11.3
NUCLEATION AND GROWTH OF STABLE PHASE IN AN ISING TYPE SYSTEM. Vitaly A. Shneidman, Kenneth A. Jackson and Kirk M. Beatty, Dept of Materials Science and Engineering, University of Arizona, Tucson, AZ.

Large systems (up to $4 \cdot 10^6$) of nearest-neighbor interacting spins driven by a Glauber-type dynamics were studied as models for a first order phase transition on two-dimensional square and hexagonal lattices. Such systems are unique due to the availability of exact values of the interfacial energy, known from the Onsager solution and later developments, and the known Wulff shapes of macroscopic nuclei. The primary goal of the study was to verify thermodynamic and kinetic aspects of the conventional nucleation and growth descriptions which are associated with the formation of critical nuclei, motion of the interface, growth and decay of individual nuclei, and with their size distributions. The role of time-dependent nucleation was highlighted, and the overall kinetics of the phase transition were examined. The latter turn out to be remarkably consistent with the Kolmogorov-Avrami description, but the classical theory of nucleation requires certain modifications in order to comply with observation data.

9:45 AM E11.4
MODELLING OF NON-RANDOM NUCLEATION PROTOCOLS. Eloi Pineda and Daniel Crespo, Dept. de Física Aplicada, Universitat Politècnica de Catalunya, Barcelona, SPAIN; Trinitat Pradell, ESAB, Universitat Politècnica de Catalunya, Barcelona, SPAIN.

Non-random nucleation is a subject of high interest in crystallization processes because nucleation rates may change along the transformation in the neighbourhood of a growing grain. In this case the direct application of the KJMA kinetics does not give an adequate description of the transformation kinetics. This is due to the fact that in these systems the first of the two main hypotheses over which the KJMA formalism is grounded, namely random nucleation and isotropic growth, is not accomplished. In this study an expression for the extended volume, considering the non-random nucleation effect, is obtained. The results show that although this is not enough to obtain a complete description of the transformation, the discrepancies

between the approximation and Monte-Carlo simulations of non random nucleation processes are small. The formalism has been applied to several cases, including the extreme situation where nucleation is completely inhibited in a region around the growing grains.

10:30 AM *E12.1
EXPERIMENTAL INVESTIGATIONS ON THE NUCLEUS SIZE IN VERY VICINITY OF SOLUBILITY LIMIT BY THE COMPOSITION GRADIENT METHOD. Toru Miyazaki, Dept. of Materials Science and Engineering, Nagoya Institute of Technology, Nagoya, JAPAN.

A comprehensive description of phase transformations should be realized in the form of the three dimensional diagram having the temperature(T), time(t) and composition(c) axes. The sections parallel to the temperature(T) and the com-position (c) axes and parallel to the temperature(T) and the time(t) axes are well known as the phase diagram and the TTT diagram, respectively. A section par-allel to the composition(c) and time(t) axes is also important as well as the phase diagram and the TTT diagram, nevertheless it has not received attention yet. The c-axis is an important element of the T-t-c diagram as above described, so the experiments whose variable is composition c should be conducted. In the present, a new experimental method to determine the phase boundary and phase equilibrium is accomplished by utilizing the macroscopic composition gradient method recently proposed, where the solute composition changes con-tinuously so as to step over the phase boundary. The various critical phenomena at the very vicinity of phase boundary, i.e. the continuous change at the coherent binodal/spinodal line, microstructural transition at the 2nd order/disorder trans-formation, the equilibrium compositions at the interface of precipitate/matrix and the composition dependence of nucleus size at the very vicinity of solubility limit are successfully obtained for Cu-Ti, Ni-Al, Ni-Mo, Cu-Co and Ni-Al-Ti alloy sys-tems. It is expected that the composition gradient method proposed in the present will become an important experimental method of the microstructural characteriza-tion, particularly for the critical phenomena.

11:00 AM *E12.2
PHASE FIELD APPROACH TO TRANSFORMATIONS INVOLVING CONCURRENT NUCLEATION AND GROWTH. J.P. Simmons, Air Force Research Laboratory, Materials and Manufacturing Directorate, Processing Science Group, AFRL/MLLM, Wright-Patterson AFB, Dayton, OH; S. Chen, The Ohio State University, Columbus, OH; Y. Wang, The Ohio State University, Columbus, OH.

Because of its ability to handle large volume fractions and to explicitly account for elastic interactions of precipitates, the phase field method is ideally suited for modeling microstructural development in Ni-based superalloys. In its conventional formulation, nucleation is accounted for with a Langevin noise term, which allows nucleation of precipitates via composition and order parameter fluctuations. However, due to the difference in time scales of the nucleation and growth processes, this approach is limited to site saturation conditions. Since superalloy processing generally requires non-isothermal conditions, site saturation conditions cannot generally be achieved. This work presents a modification of the conventional phase field approach, which explicitly models nucleation events as a stochastic process. Under this method, the nucleation rate is treated as a function of the local alloy concentration and is matched to the mean value of the rate at which nuclei are introduced into phase field cells. This allows simulations to be performed where the undercooling is constantly changing. Recent results will be presented in terms of the effects of transformation conditions on microstructures developed.

11:30 AM E12.3
MEASURING TEMPORAL EVOLUTION OF PARTICLE SIZES USING TRANSMISSION ELECTRON MICROSCOPY AND SMALL-ANGLE NEUTRON SCATTERING: A COMPARISON. G. Muralidharan, J.E. Epperson, Argonne National Laboratory, Argonne, IL; S.L. Weber, M.J. Pollard, Haydn Chen, University of Illinois, Department of Materials Science and Engineering, Urbana, IL.

Small-angle neutron scattering (SANS) and Transmission Electron Microscopy (TEM) are two popular techniques used for the study of coarsening. Each of these techniques has its advantages and disadvantages. TEM has the advantage that it is visual but is limited in that it is primarily only an $ex - situ$ characterization technique and the sampling volume is small compared to that for SANS. SANS has the advantage that it is truly a bulk technique, is amenable to $in - situ$) measurements but has the disadvantage that the particle size has to be derived from the SANS spectra. Due to the complexities associated with the complete modeling of the SANS spectra obtained from precipitates in alloys, a simple approximation, the Guinier approximation, is commonly used to obtain characteristic particle size information from the SANS spectra. However, recently, the validity of using this approximation to obtain coarsening rates, and comparing coarsening rates obtained by using this approximation has been questioned. In the current study, we have measured the temporal evolution of particle sizes in various alloys from the Ni-Al-Si system, using both $in - situ$ SANS and $ex - situ$ TEM. The presentation will compare the coarsening kinetics obtained for these alloys using the two techniques. Role of various factors such as the particle size distribution measured using the TEM and scaling of the SANS spectra in the magnitude of differences measured in the absolute values of the coarsening rates will be outlined. The presentation will also examine the validity of comparing coarsening rates measured in different alloys using SANS. It is concluded that both techniques yield similar results, consistent with each other. The misfit strain induced coarsening rate anomalies were confirmed with both techniques. A preliminary model is suggested to explain these results. Research supported by the US Department of Energy.

11:45 AM E12.4
ATOM-BY-ATOM GROWTH: NUCLEATION, MORPHOLOGY TRANSITIONS, AND LONG-RANGE INTERACTIONS. A. Bogicevic, D.R. Jennison, Surface and Interface Sciences Department, Sandia National Laboratories, Albuquerque, NM; S. Ovesson, B.I. Lundqvist, Department of Applied Physics, Chalmers University of Technology and Göteborg University, Göteborg, SWEDEN.

The continuous drive to produce smaller and faster electronic components, cheaper and more efficient catalysts, etc., has led to radical changes in manufacturing methods. For example, the transistors and diodes in modern microchips, laserpens, and other electronical gadgets, all contain minute junctions that have been grown atom by atom. There is thus a great incentive to study interactions amongst deposited adatoms. In this talk, I will treat three growth-related topics. First, I will present results from ab $initio$ kinetic Monte Carlo simulations that resolve three current issues in epitaxial growth: (i) The appearance of compact triangular islands during growth on close-packed surfaces is shown to be linked to anisotropy in corner diffusion rather than edge diffusion. (ii) The absolute correlation between the orientation of dendrites grown at low T and triangular islands grown at higher T is thus evident. (iii) An explanation is given to why in some systems dendrites grow fat before turning compact. Dimers nucleate larger islands, strongly influencing early stages of growth. They also affect the island density, and can thus easily throw off STM measurements of adatom diffusivity using nucleation theory. Despite detailed FIM and STM studies, dimer motion on open (100) metal surfaces is largely unresolved. I will here present first-principles calculations for atom-by-atom and concerted hopping of dimers on (100) surfaces of metals, and discuss the generality of obtained results. Lastly, I will present extensive first-principles calculations aimed at quantifying the strength of indirect adatom interactions, mediated elastically (through the substrate) and electronically (via Friedel oscillations). Specifically, I will report the magnitude of oscillations in adatom diffusion versus adatom separation for Al/Al(111) and Cu/Cu(111) using up to 4 nm long super-cells. I will then elaborate on whether these results can affect the island density enough to explain the anomalously low diffusion prefactors deduced indirectly for some metal systems from STM via nucleation theory.

1:30 PM *E13.1
THE DYNAMICS OF OSTWALD RIPENING IN ELASTICALLY STRESSED SOLIDS. N. Akaiwa, National Research Institute for Metals, Tsukuba, JAPAN; K. Thornton and P.W. Voorhees, Department of Materials Science and Engineering, Northwestern University, Evanston IL.

Elastic stress is present in a wide variety of two-phase solids. A major challenge in predicting the evolution of microstructures in these systems is that the difference in lattice parameters between the particle and matrix engenders a long-ranged elastic stress field. Unlike

stress-free systems, where the evolution of the microstructure is driven by a decrease in the total interfacial energy of the two-phase mixture, the ripening process in these materials is driven by a decrease in the sum of the elastic and interfacial energies. This change can give rise to qualitatively new phenomena, such as inverse Ostwald ripening wherein small particles grow at the expense of large particles, large-scale particle migration and particle shape bifurcations. Through the use of boundary integrals and the fast multipole method, it is now possible to determine the morphological evolution of many thousands of elastically and diffusionally interacting particles. We can thus make predictions on the evolution of statistically averaged properties of these coarsening ensembles such as the exponent of the temporal power law for the average particle size and evolution of the spatial correlations between particles. A discussion of these results will be given.

2:00 PM *E13.2
ATOMISTIC MODELING OF GRAIN BOUNDARY MIGRATION. D.J. Srolovitz, Princeton Materials Institute, Princeton University, Princeton, NJ; M. Upmanyu, Dept. of Materials Science & Eng., University of Michigan, Ann Arbor, MI; L.S. Shvindlerman, Institute of Solid State Physics, Chernogolovka, RUSSIA; G. Gottstein, IMM, RWTH, Aachen, GERMANY.

All coarsening processes and growth processes associated with first-order phase transitions involve some form of interface migration. Our understanding of boundary migration is extremely rudimentary except in a few special cases since interface mobilities are commonly determined on the atomic level. I will present recent atomistic (molecular dynamics) simulation results examining one class of interface motion - namely, grain boundary migration. I will focus on the variation of grain boundary mobility with boundary misorientation and temperature. The misorientation dependence is key to determining texture evolution during thermal processing since boundary mobilities routinely vary by several orders of magnitude at a constant temperature. Although there appears to be a cusp in the activation energy vs. misorientation plots at special misorientations, the actual boundary mobility shows a relatively smooth variation. I will also present some recent results on the effect of triple junctions (where three grain boundaries meet) on curvature driven growth. The present results answer several fundamental questions regarding boundary migration and raise several new ones.

2:30 PM E13.3
IN SITU STM OBSERVATION OF THE SPIRAL GROWTH IN THE EPITAXIAL Fe FILMS ON MgO(001). Agus Subagyo, Hokkaido Univ, Dept of Electronics and Information Engineering, Sapporo, JAPAN; Kazuhisa Sueoka, Hokkaido Univ & PRESTO-JST, Sapporo, JAPAN; Koichi Mukasa, Hokkaido Univ & CREST-JST, Sapporo, JAPAN.

Here we report on the founding of the presence of spiral growth on the epitaxial growth bcc Fe films on MgO (001) substrates. We studied the growth temperature dependence of the growth and structural properties of this material by means of scanning tunneling microscopy (STM) and reflection high energy electron diffraction (RHHED). Fe films were deposited by molecular beam epitaxy (MBE) system on mechanically polished MgO (001) substrates up to 100 $\mathring{A}$ at a growth temperature ranged between room temperature and 320°C. The deposition rate was typically 0.5 ML/min.(ML: monolayer; 1 ML=1.433 $\mathring{A}$). The flux of Fe atoms being directed along the Fe[110] direction. The pressure during deposition never exceeded 3.0×10^{-8} Pa. As the growth temperature is increased, the Fe islands became squarer forming atomically flat terraces and the rms surface roughness decreased. The spiral growth observed on the films grown at or above a temperature of 220°C, and above a film thickness of 50 $\mathring{A}$. At this temperature, RHHED patterns showed a presence of surface reconstruction, which also clearly observed by STM. This talk will discuss the mechanism of the presence of spiral growth and the possible surface reconstruction on the epitaxial bcc Fe on MgO (001) related with growth temperature and surface diffusion.

2:45 PM E13.4
CONTINUUM MODELS OF FACETING. Navot Israeli, Daniel Kandel, Weizmann Inst of Science, Dept of Physics of Complex Systems, Rehovot, ISRAEL.

Modeling of surface dynamics below the roughening transition is complicated by the appearance of facets. These facets are a manifestation of the cusp singularities in the surface free energy at high symmetry orientations. On the microscopic level faceting is well understood in terms models which follow the motion of atomic steps. However, there is currently no macroscopic model which treats faceting and at the same time is consistent with the microscopic step flow dynamics. Such a model would be useful, since step flow models are usually too complicated to supply a comprehensive account of the large scale surface evolution. To this end we study several surface

morphologies with facets. We first study these systems by step flow models from which we derive exact continuum models for the surface evolution. In this framework faceting is understood in a consistent way both on the microscopic and the macroscopic levels. On this basis we suggest a general scheme for dealing with facets on a macroscopic level.

SESSION E14: NANOSYSTEMS
Chair: Daniel Crespo
Wednesday Afternoon, December 1, 1999
Room 210 (H)

3:30 PM *E14.1
FIRST-PRINCIPLES THEORY OF COHERENT PRECIPITATE SHAPES IN ALUMINUM ALLOYS. C. Wolverton, Ford Research Laboratories, Dearborn, MI.

A first-principles theoretical approach has been developed for studying coherent precipitate shapes in aluminum alloys. [1] This atomistic approach, which represents an alternative to empirical potential or continuum models, involves mapping a large set of first-principles total energies onto a "mixed-space cluster expansion" taking into account both strain and interfacial energies. This cluster expansion involves generalized Ising-like terms (with long-ranged pair interactions and short-ranged 3- and 4-body terms) and the coherency strain which possesses the correct anisotropic and anharmonic elastic response of a coherent A/B interface. The effects of finite temperature are incorporated via Monte Carlo simulations thus treating systems of ~ 200 Angstroms with first-principles accuracy. Examples of this approach are shown for studying the equilibrium shapes of coherent precipitates in size-mismatched aluminum alloys, such as Al-Cu and Al-Mg. In Al-Cu, disc-shaped (001) plates of Cu are found as the equilibrium precipitates, which are the well-known GP zones. However, competition between the interfacial energy around the rim of the disc and the driving force for a theoretically-predicted coherent ground state leads to a size-dependent transition of the equilibrium precipitate shape, explaining the observed GP1/GP2 transition. In Al-Mg, an ordered L12 phase is predicted as the coherent ground state, and thus precipitates in this system are found to form in this ordered structure, in agreement with observations of precipitation in this system.
[1] C. Wolverton, Phil. Mag. Lett. (in press, 1999).

4:00 PM E14.2
SIMULATION OF MORPHOLOGY AND THERMAL FLUCTUATION OF METALLIC FINE PARTICLES. Yoshiaki. Kogure and Masao Doyama, Teikyo University of Science and Technology, Uenohara, Yamanashi, JAPAN.

Morphology and thermal fluctuation of fine particles have been investigated by means of molecular dynamics simulation. The particles are consisted of 1000−10000 atoms of noble metal (Cu, Ag, Au). For the atomic interaction EAM potential developed by the present authors[1] and two body (Lennard-Jones) potential are adopted, and both results are compared. As an initial condition of model system atoms are arranged in fcc structure with [100] surfaces. The temperature of the system is elevated to 3000 K and the system is melted with spherical surface. Then the system is cooled down to 0 K rapidly or slowly and the particles are stabilized. The surface morphology of the particle is investigated by highlighting the surface atoms through the potential energy. The local crystalline order is also calculated to visualize the atomic configuration inside of the particle. From the relative positions of neighboring atoms, atoms in the particle are distinguished to fcc, hcp, and other structures by this method. The slowly cooled particles have a crystalline nature. Large area of the surface is consisted of [100] crystal face. Inside of the particle is consisted of several grains of fcc structure. The rapidly cooled particles are rather glassy and disordered. The degree of crystallinity of disordered particles are evaluated from the radial distribution function. The temperature of the particles are elevated and time evolution of the particle morphology of is monitored. Even the temperature is very lower than melting temperature, for example 500 K, the particle morphology is found to be fluctuating especially for small particle. This may be due to the intrinsic property of small atomic system described by the statistical mechanics. The relation between the fluctuation and the local atomic motion is investigated.
[1] M. Doyama and Y. Kogure, Radiation Effects and Defects in Solid 142, 107 (1997)

4:15 PM E14.3
KINETICS OF GRAIN GROWTH IN THE NANOCRYSTALLINE REGIME. C.E. Krill, University of the Saarland, Dept of Physics, Saarbruecken, GERMANY.

The conventional view of grain growth as a transformation resulting

from curvature-induced motion of grain boundaries was developed to explain the kinetics of growth measured in samples with grain sizes larger than 1 μm. The growing technological importance of materials with much smaller grain sizes suggests that the standard theory should be tested for its applicability to greatly reduced length scales, such as those found in nanocrystalline specimens. Recent theories predict that a reduction in grain size should be accompanied by the manifestation of new factors influencing the kinetics of grain growth, such as the motion of triple junctions [1] and the annihilation of excess volume [2]. Likewise, the long-discussed (but never observed) "stochastic" mechanism for grain growth, which involves random jumps of atoms across grain boundaries, is predicted to become increasingly important in the limit of small grain size [3]. These size-dependent factors have a drastic influence on the exponent characterizing the growth kinetics and should, therefore, be experimentally observable. We describe initial measurements of the kinetics of grain growth in nanocrystalline samples by x-ray diffraction techniques, the results of which are incompatible with a stochastic mechanism for boundary motion. We discuss the reasons underlying this observation as well as the relevance of such measurements to the other factors postulated to control grain growth in the nanocrystalline regime.

[1] U. Czubayko, V.G. Sursaeva, G. Gottstein and L.S. Shvindlerman, *Acta mater.* **46** (1998) 5863.
[2] Y. Estrin, G. Gottstein and L.S. Shvindlerman (preprint).
[3] D.T. Wu, *Mater. Res. Soc. Symp. Proc.* **343** (1994) 55.

4:30 PM E14.4
COMPOSITION MODULATION, NANOPHASE SEPARATION AND PATTERN FORMATION IN A BINARY EPILAYER. Z. Suo and W. Lu, Mechanical and Aerospace Engineering Department and Materials Institute, Princeton University, Princeton, NJ.

When a thin binary layer grows epitaxially on an elemental substrate, the composition often modulates in the plane of the layer. The layer may even demix when the bulk of the same composition is miscible. Sometimes the layer separates into two phases, forming periodic stripes or other regular patterns. The size of the separated phases may be in the range 1-100 nm, and stable against coarsening on annealing. This paper develops a thermodynamic framework to study these remarkable phenomena. The free energy of the epilayer-substrate composite is a sum of the surface energy and the bulk elastic energy. For an epilayer less than a few monolayers thick, the excess energy cannot be attributed to individual sources of superficial misfit. Instead, we lump the epilayer and adjacent monolayers of the substrate into a single superficial object, and specify the excess surface energy for the object. The surface energy density is taken to be a function of the composition, the elastic strain, and the composition-gradient. The composition dependence prescribes the relative stability of the phases. The strain dependence couples the phase morphology in the epilayer to the elastic deformation in the substrate, mediating a long range interaction that refines the phases. The composition-gradient dependence provides a continuum description of the phase boundary energy, mediating a short range interaction that coarsens the phases. It is this competition that stabilizes the phase size. We report analytical and numerical results of this model.

4:45 PM E14.5
SCALING OF THE ISLAND SIZE DISTRIBUTION OF DIFFUSING ISLANDS. Daniel Kandel, Weizmann Inst of Science, Dept of Physics of Complex Systems, Rehovot, ISRAEL.

Experiments show that two dimensional islands can diffuse and coalesce on crystalline surfaces. We studied the evolution of the island size distribution of such systems in the framework of a mean field model, which takes into account the various possible microscopic mechanisms responsible for island diffusion. Numerical integration of the equations shows that the island size distribution exhibits a scaling behavior. An analytical scaling analysis predicts the correct values of the scaling exponents and yields an integro-differential equation for the scaling function. We showed that this equation admits a one parameter family of mathematically valid scaling solutions. Despite this, the kinetics reaches a unique island size distribution function, independent of initial conditions. We propose a kinetic mechanism for the selection of the island size distribution from the family of solutions, and verify its validity numerically.