SYMPOSIUM I

New Methods, Mechanisms, and Models of Vapor Deposition

April 24 – 26, 2000

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* Invited paper

SESSION I1: NEW METHODS OF VAPOR DEPOSITION I
Chairs: Haydn N. G. Wadley and Joseph E. Greene
Monday Morning, April 24, 2000
Golden Gate A3 (Marriott)

8:30 AM *I1.1
FILM GROWTH UNDER HIGHLY KINETICALLY CONSTRAINED CONDITIONS: H-MEDIATION, SURFACE SEGREGATION, AND ULTRA-HIGH DOPING DURING $Si_{1-x}Ge_x$ ALE AND GAS-SOURCE MBE. Joe Greene, Materials Science Dept. and MRL, Univ. of Illinois, Urbana, IL.

Surface reaction pathways and kinetics of $Si_{1-x}Ge_x$ growth on Si(001) by both gas-source MBE (GS-MBE) and atomic-layer epitaxy (ALE) from Si_2H_6/Ge_2H_6 mixtures have been investigated using a combination of *in-situ* RHEED, EELS, STM, STS, TPD, and AES together with post-deposition TEM, HR-XRD, XTEM, and electronic transport measurements. Film growth data are well described by models containing separate reaction steps for dissociative chemisorption, surface reactions, and hydrogen desorption. For UV-photostimulated ALE, hydrogen termination provides internally self-limiting kinetics and allows epitaxial growth at room temperature and below.
The results of isotopically-tagged D_2 temperature-programmed desorption (TPD) experiments were used to model temperature-dependent H-mediated effects of high B coverages on the growth kinetics of B ultra-high doped $Si_{1-x}Ge_x(001)$, up to $1.5x10^{22}$ cm^{-3} (30 at%), through changes in B-induced surface reconstruction and back-bond charge transfer, and to determine Ge segregation kinetics as a function of x and steady-state H coverage during GS-MBE. Excess incorporated B does not precipitate out of solution as commonly supposed. Rather, our recent NEXAFS and HR-XRD results, carried out at the Synchrotron Radiation Center in Stoughton, show it is incorporated as sp^2 bonded dimers with trigonal symmetry on substitutional Si sites. The dimers are bond-saturated and thus electrically neutral. Further, they have very low charge scattering cross-sections.

9:00 AM *I1.2
ATOMIC LAYER DEPOSITION (ALD) OF Ta FOR INTER-CONNECT APPLICATIONS. S.M. Rossnagel, IBM Research, Yorktown Heights, NY; A. Sherman, F. Turner, Sherman and Associates, Menlo Park, CA.

Interconnect structures for semiconductors require the usage of thin, conformal films which function as diffusion barriers for in- and out-diffusion, adhesion layers, and seed or preferential deposition layers for subsequent materials. A typical example is the use of a thin, conformal Ta film on the walls of a dielectric trench or via which reduces or eliminates out-diffusion of the primary conductor, usually Cu, into the dielectric. Atomic Layer Deposition is a known technique which is intrinsically conformal and is appropriate for this application. Plasma-enhancement of the process allows deposition at significantly lower temperatures than conventional CVD, which is a requirement for low-k dielectrics. Tantalum films deposited at 25-250 C using ALD with a TaCl5 precurser and atomic hydrogen as the reactive species at up to a rate of 1.67 Ang/cycle are amorphous, conformal, and show moderate or controllable levels of impurities; primarily oxygen and a small level of Cl. The films are conformal at aspect ratios of up to 5:1. The process scales to manufacturing dimensions and applications and will facilitate the extension of inerconnect technology beyond (below) 100 nm dimensions.

9:30 AM I1.3
IN-SITU X-RAY DIFFRACTION DURING SPUTTER DEPOSITION OF THIN FILMS. Steven M. Yalisove and John C. Bilello, University of Michigan, Department of Materials Science and Engineering, Ann Arbor, MI.

Physical vapor deposition via thermal evaporation has been studied for some time with sophisticated in-situ electron beam techniques with phenomenal success. Yet, the far more commercially used deposition technique of magnetron sputtering has not had the advantage of similar in-situ characterization. Electron methods simply dont work at 20 mtorr in a plasma. Light scattering has been used to some degree but can only discern large scale features corresponding to very rough surfaces or to overall surface curvature (recent work here has been very exciting with regard to evolution of average stress in films). X-rays do not really care whether or not they travel through a plasma or a gas. We have designed and constructed a growth and analysis system by coupling an 18KW rotating anode x-ray source to a magnetron sputtering chamber. X-rays, from the line source of the anode, are directed towards a beryllium window in the chamber, through a slit system, and impinge at a grazing angle onto a growing film. Scattered x-rays are collected on the other side of the chamber, through a beryllium window and analyzed by an Inelo position sensitive detector. A complete 2 Θ diffraction pattern can be collected in as little as 1 second (for a thick high Z film). Hence, phase, microstructure, strain, and texture information can be inferred while the film is growing. Examples of recent work with this system will be presented including Ta, Cr, and Cr_xN_y sputtered films.

10:15 AM I1.4
SURFACE CATALYZED PHOTO-ASSISTED MOCVD OF COBALT FILMS FOR ENHANCED CONTROL OF MAGNETIC PROPERTIES. Mariana Chioncel, Peter Haycock, Feodor Ogrin, Brian Ruthven, John Bull, Keele Univ, School of Chemistry and Physics, Staffordshire, UNITED KINGDOM; Steve Hoon, Manchester Metropolitan Univ, Dept of Environmental and Geographical Sciences, Manchester, UNITED KINGDOM.

The magnetic properties of thin films of cobalt are extremely dependent upon the microstructure and the surface and interface stoichiometry. Here we present a means of controlling these properties through growth of cobalt films by metal-organic chemical vapor deposition (MOCVD). This has enabled repeatable production of films with a wide range of magnetic behavior. MOCVD is not widely used for fabrication of cobalt films. However, previous studies have identified suitable precursors for their deposition and corresponding process parameters. We have built on these results so as to enable control of the magnetic properties of the MOCVD films. Our initial work involved pyrolytic decomposition of the precursor vapor. However, in order to change the growth mode we subsequently made use of a UV lamp to induce photolytic decomposition of cyclopentadienylcobalt dicarbonyl. This enabled the optimum deposition temperature to be reduced by 230° to 120°. The microstructures of films grown by pyrolysis at 350° and photolysis at 120° are similar, but the latter material is largely amorphous, as opposed to a high degree of crystallinity and a strong (00.1) texture in the former case. Some films produced by pyrolysis exhibited a small inverted magnetic hysteresis loop when the magnetic field was applied along the film normal. This effect was of similar magnitude to that noted previously, but very rarely, in other materials. Photo-assisted deposition at 120° has allowed production of films exhibiting very large inverted hysteresis loops, giving opportunity for a more thorough investigation of the phenomenon. The effect is attributable to the magnetic interaction between pure cobalt in the middle of the film and oxide layers at the surface and the interface with the glass substrate. The repeatability of production of films with a large inverse hysteresis is due to the self-limiting nature of the surface catalyzed photolytic decomposition mechanism.

10:30 AM I1.5
ATOMIC-SCALE MODELING OF PLASMA DEPOSITION OF SILICON THIN FILMS. Shyam Ramalingam, Stephen P. Walch, Eray S. Aydil and Dimitrios Maroudas, UC Santa Barbara, Santa Barbara, CA.

A systematic computational analysis is presented of growth of hydrogenated amorphous silicon (a-Si:H) films on H-terminated Si(001)-(2x1) substrates over the temperature (T) range 500 K ¡= T ¡= 773 K. Molecular-dynamics (MD) simulations of repeated SiH_x (x=1,2,3) radical and H atom impingement is used to grow films at MD-fast growth rates and identify important surface chemical reactions that govern the deposition mechanisms. The reaction energy landscapes are computed along the surface reaction paths and the corresponding reactant, transition-state, and product energy levels are calculated accurately based on density functional theory. The resulting database can then be used as input to stochastic dynamical simulations of a-Si:H film growth from SiH_4 containing discharges at realistic deposition rates. Surface reactions with the SiH_3, SiH_2, and SiH radicals have been identified and analyzed that include abstraction of surface hydrogen atoms through Eley-Rideal mechanisms, insertion reactions accompanied by breaking of Si-Si bonds, surface migration, H transfer between adsorbed radicals and SiH_4 desorption, as well as formation of larger clusters through reactions between adsorbed surface species. A reaction between two adsorbed surface dihydride species to form Si_2H_4 surface species is studied in detail and the resulting configurations are compared with recent experimental measurements. Sticking probabilities are computed for all the impinging radicals: a 96% sticking probability for SiH is in very good agreement with recent experimental data. Surface H abstraction reactions by impinging H atoms and H_2 desorption from the surface are demonstrated and analyzed. The evolution of the MD-deposited film structure, composition, and morphology also is discussed. The surface hydride content of films grown by MD over several nanoseconds are compared with our ATR-FTIR spectroscopy data on PECVD-grown a-Si:H films. The comparisons are used to discuss our current understanding of the deposition mechanism.

10:45 AM I1.6
PARALLEL DETECTING, SPECTROSCOPIC ELLIPSOMETER FOR INTELLIGENT PROCESS CONTROL OF CONTINUOUSLY

DEPOSITED CIGS FILMS. L.J. Simpson and L.A. Gonzales, ITN Energy Systems, Inc., Wheat Ridge, CO.

Advanced materials processing involves active control of fabrication and real-time monitoring of the final product. Sensors must be an integral part of the overall material processing system. ITN Energy Systems, Inc. and associates have developed a Parallel Detection, Spectroscopic Ellipsometer (PDSE) sensor for in-situ, real-time characterization and process control of multi-layered vapor deposited films. By measuring changes in the polarization state of reflecting light as a function of wavelength (250 to 1700 nm), the PDSE sensor determines the complex reflectance and/or the ellipsometric amplitude and phase. The PDSE provides cost-effective in-line sensing for film process control through detection of critical product variables that directly relate to film performance including: film thickness, optical excitation states, impurity concentrations, conductivity/ resistance, intermixing at interfaces, microstructure, surface roughness, void fraction, defects, and grain size. The PDSE sensor is an optical probe with no moving parts that can measure the optical properties of thin films in less than 20 msec with sensitivity to films less than a monolayer in thickness. To date, most of our efforts have involved instrumentation design, construction, and implementation into a $CuInGaSe_2$ (CIGS) deposition chamber. We have used this PDSE system to provide real time process control of vapor deposited CIGS films on a continuous flexible substrate. Initial results from CIGS films indicate that the PDSE has the sensitivity and accuracy to provide intelligent process control. The challenge is to develop interpretive algorithms; the amount and quality of information required will determine their complexity. In addition, with the inception of in-situ, real-time monitoring, we hope to enable minimal data analysis approaches (D. E. Aspnes, Appl. Phys. Lett. 62, 1993) that provide extremely useful information with minimum interpretive algorithm development.

11:00 AM I1.7
REAL TIME SUBSTRATE TEMPERATURE CONTROL BY EMISSIVITY COMPENSATED PYROMETRY DURING InGaAsP/INP GROWTH ON PRODUCTION SCALE ROTATING DISC MOVPE REACTORS. J. Ramer, B. Patel, M. Schurman, V. Boguslavskiy, A. Gurary, A. Patel, Emcore Corporation, Somerset, NJ.

Long term control of the substrate temperature in production scale MOVPE reactors is the most significant issue effecting yields in highly temperature sensitive epitaxial growth processes. Recent advances in non-contact emissivity compensated pyrometry wafer temperature measurements have allowed the development of a novel multi-wafer (6x2) rotating disc MOVPE reactor with real time substrate temperature control. With this system, the substrate temperature is a directly controlled process variable, in contrast to some conventional MOVPE systems which use thermocouples for process temperature control. In addition to controlling the absolute temperature of the substrates, the temperature uniformity across the substrates is also controlled by pyrometry. This provides for a uniform temperature ($\pm$1.5 C) across the substrates independent of the flow conditions within the reactor. Thermal uniformity is also automatically maintained during temperature ramping. The highly temperature sensitive quaternary InGaAsP is used as an epitaxial metric for this novel control system, to demonstrate the advantages of pyrometry controlled substrate temperature. These advantages include: excellent long term substrate temperature reproducibility; invariance of substrate temperature to substrate doping level; the ability to transfer processes from one type of wafer carrier or reactor to another with minimal adjustment.

11:15 AM *I1.8
ELECTRON BEAM VAPOR DEPOSITION FOR HTSC TAPE MANUFACTURE. Jonathan Storer, 3M Company, Mendota Heights, MN.

3M is developing technologies for making YBCO tape on textured metal substrates. Electron beam co-evaporation has been chosen as the superconductor deposition method. Textured substrates are made by the RABiTS and IBAD methods.
Modeling has been used to both understand the IBAD and YBCO evaporation processes and to develop controls for them. The talk will describe the overall goals of 3M's HTSC program and present insights into the use of selected examples from the suite of models which have been employed.

11:45 AM I1.9
LATERAL EPITAXIAL OVERGROWTH OF GaSb ON GaSb AND GaAs SUBSTRATES BY METALORGANIC CHEMICAL VAPOR DEPOSITION. S.S. Yi, D.M. Hansen, T.F. Kuech, Univ of Wisconsin-Madison, Dept of Chemical Engineering, Madison, WI; C.K. Inoki, D.L. Harris, T.S. Kuan, SUNY-Albany, Dept of Physics, Albany, NY.

GaSb-based compound semiconductors are of great interest for infrared optoelectronic devices over the ranges from 1.24 μm for AlGaAsSb to 4.4 μm for GaInAsSb, and high-speed electronic devices. In order to measure electrical properties of epilayers, it is necessary to isolate the epilayers electrically from the substrate. Since semi-insulating GaSb substrates are not available, GaAs substrates are normally used in many electronic applications. A principal concern in the growth of GaSb on GaAs substrates is the large, 8% lattice mismatch that leads to a high threading dislocation density. The dislocation density can be reduced by growing an appropriate thin, low temperature GaSb buffer layer. However, the optimal growth condition for such an initial buffer layer has not well established yet. The lateral epitaxial overgrowth of GaSb on GaAs substrates is of particular interest because of the local lateral growth of GaSb material that can potentially be free of threading dislocations. We demonstrate, to our knowledge, the first successful lateral epitaxial overgrowth of GaSb on GaSb and GaAs substrates patterned with SiO_2 or Si_3N_4 films by metalorganic chemical vapor deposition using trimethylgallium and trimethylantimony. The grown layers are characterized by scanning electron microscopy, transmission electron microscopy, and photoluminescence. Transmission electron microscopy measurements show that coalesced films grown on GaSb substrates exhibit defect-free materials, while those on GaAs substrates show regions possessing various defect structures originating from large lattice mismatch and thermal stress.

SESSION I2: NEW METHODS OF VAPOR DEPOSITION II
Chairs: Jennifer J. Zinck and David G. Meyer
Monday Afternoon, April 24, 2000
Golden Gate A3 (Marriott)

1:30 PM I2.1
CHEMICAL VAPOR DEPOSITION COATING FOR MICRO-MACHINES. S.S. Mani, J.G. Fleming, J.J. Sniegowski, M.P. de Boer, L.W. Irwin, J.A. Walraven and J. Jakubczak.

A novel low pressure chemical vapor deposition coating for microengines has been developed. The process deposits a thin extremely conformal layer of tungsten. The deposition process is self limiting and selective to Si. The attributes of excellent step coverage and uniformity makes this coating process very attractive for microelectro mechanical systems (MEMS). Tungsten provides a hard, wear resistant, chemically resistant protective layer of coating selective to Si making it desirable for micromachine applications with wearing surfaces. The selective chemical vapor deposition of tungsten is accomplished through silicon reduction of WF6, which results in a self-limiting reaction. This selective deposition of W only on polysilicon surfaces prevents electrical shorts. Further, the self-limiting nature of this selective W deposition process ensures the consistency necessary for process control. The selective tungsten is deposited after the removal of the sacrificial oxides to minimize process integration problems. This tungsten coating adheres well and is hard and conducting, requirements for device performance. Furthermore, since the deposited tungsten infiltrates under adhered silicon parts and the volume of W deposited is less than the amount of Si consumed, it appears to be possible to release stuck parts that are contacted over small areas such as dimples or hubs. Results from tungsten deposition on MEMS structures will be presented. The effect of wet and vapor phase cleans prior to the deposition will be discussed along with other process details. Endurance of the W coating is important, especially in applications where wear may occur. Tungsten CVD is used in the integrated-circuit industry, which makes this approach manufacturable. The United States Department of Energy under contract DE-AC04-94AL85000 supported this work. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

1:45 PM *I2.2
ON THE CHALLENGES AND OPPORTUNITIES OF SENSING MATERIAL GROWTH WITHIN PRODUCTION DEPOSITION TOOLS. J.C. Bean, S. Kanakaraju and M. Lau, Department of Electrical Engineering, University of Virginia, Charlottesville, VA.

Scanning probe microscopy has yielded extraordinary advances in our ability to characterize surfaces at the atomic scale. These advances are paralleled by improvements in computational methods and platforms that now yield realistically complex multi-scale models of deposition processes. Combining these developments, it might now be possible to sense the dynamic state of an atomic surface and then consult with models to analyze the path of the deposition process. Together, this real-time information might allow us to tweak the growing material towards particularly unique and desirable final configurations. What we are largely missing are sensors that can provide atomic scale information without, themselves, compromising

the commercial deposition process. In a manufacturing environment, sensors cannot shadow the deposition process or contaminate the material, they cannot add significantly to the complexity of the deposition tool or require that tool's extensive redesign. Importantly (at least over the long term) the sensors cannot even require us! That is, highly trained (and paid) individuals to operate and interpret their data. These restrictions suggest that simplified, stand-off, sensors may provide incomplete information, hinting at a surface configuration that would then be corroborated, in real-time, with models and other process databases. This talk will review both the challenges and opportunities we face in developing these idealized in-situ material sensors. We will draw on both examples from the literature and on our own experience in a DARPA project combining modelers, sensers and commercial deposition tool designers.

2:15 PM I2.3
VAPOR PHASE SYNTHESIS OF II-VI SEMICONDUCTOR NANOPARTICLES IN A COUNTERFLOW JET REACTOR.
D. Sarigiannis, J.D. Peck, T.J. Mountziaris, SUNY at Buffalo, Dept. of Chemical Engineering, Buffalo, NY; G. Kioseoglou, A. Petrou, SUNY at Buffalo, Dept. of Physics, Buffalo, NY.

Semiconductor nanoparticles have been synthesized in liquid media for applications ranging from LEDs and photovoltaics, to fluorescent biological labels [1,2]. However, the current technology employed in the semiconductor industry favors gas phase synthesis that can be easily integrated with existing processes and equipment. In this paper we present a novel technique for synthesis of crystalline nanoparticles of compound semiconductors by exploiting gas-phase condensation reactions in a counterflow jet reactor. The synthesis of crystalline ZnSe nanoparticles has been demonstrated using this technique and experiments are currently under way to synthesize and study nanoparticles of ternary compounds (e.g., ZnSSe) and diluted magnetic semiconductors (e.g., ZnFeSe). The counterflow jet reactor consists of two vertical coaxial jets inside a cylindrical chamber. The upper jet carries hydrogen selenide diluted in hydrogen and the lower jet carries vapors of dimethylzinc-triethylamine adduct also diluted in hydrogen. These precursors were chosen because of their high reactivity with each other, even at room temperature [3]. The gases entering from the upper and lower jets form a stagnation flow pattern at the center of the reactor and then flow radially towards the exit. Particles are produced near the stagnation point where the gases mix by diffusion and react in a laminar flow field. The radial flow to the exit is confined between two horizontal parallel plates. The particles were captured by impact, using silicon, glass and sapphire substrates located perpendicular to the radial flow field. Particle characterization was performed using (1) Scanning and Transmission Electron Microscopy to determine size, morphology and crystallinity, (2) Energy Dispersive Analysis of X-rays for chemical analysis, (3) X-ray Diffraction for structural characterization, (4) Raman [4] and transmission spectroscopies to determine degree of crystallinity, particle size and band structure. The effects of processing conditions (such as reactor pressure and temperature, inlet flow rates and precursor concentration at the inlet) on the size distribution and the properties of the particles will be discussed. This novel technique of nanoparticle synthesis appears to be very promising for producing single-crystalline nanoparticles of a variety of II-VI and III-V semiconductors. 1. Alivisatos, A.P., Electrical Studies of Semiconductor Nanocrystal Colloids. MRS Bulletin, v 23, n2, Feb. 1998. p 18-22 2. Bruchez, M. Jr., Moronne, M., Gin, P., Weiss, S., Alivisatos, A.P., Semiconductor Nanocrystals as Fluorescent Biological Labels. Science, v 281, September 25, 1998. p 2013-2015. 3. Peck, J., Mountziaris, T.J., Stoltz, S., Petrou, A., Mattocks, P.G., Metalorganic Vapor Phase Epitaxy of Zn(1-x)Fe(x)Se films. Journal of Crystal Growth. v170, 1997 p 523-527. 4. Pollak, F.H., Tsu, R., Raman Characterization of Semiconductors Revisited, SPIE v 452, 1983. p 26-43.

3:00 PM *I2.4
GETTING WHAT YOU NEED: TOWARDS A CLASS OF USEFUL REAL TIME IN SITU PROBES OF FILM GROWTH FROM THE VAPOR PHASE.
Harry A. Atwater, R.T. Brewer, D.A. Boyd, D.G. Goodwin, A.J. Rosakis, California Institute of Technology, Pasadena, CA; Y. Chen, New York University, New York, NY.

Considerable progress has recently occurred in the development of in situ probes that provide truly useful real-time chemical, crystallographic, thermal and mechanical information in vapor deposition processes. These include new, highly efficient computational approaches to obtaining real time surface information from dynamical and kinematic reflection high energy electron diffraction (RHEED) simulations coupled to RHEED measurements for single crystal and polycrystalline films. Surface chemical information can be obtained with submonolayer sensitivity at long working distance in real time from spectral analysis of RHEED electrons. In addition, optical techniques that provide extremely useful thermal, elastic and chemical information in the high pressure ambients present in chemical vapor deposition will be discussed. These include thermal and vibrational measurements derived from Fourier transform infrared (FTIR) spectroscopy and full-wafer film strain maps derived from coherent gradient sensing spectrometry.

3:30 PM I2.5
PARAMETER MODELING OF TEMPERATURE PROFILES ACROSS SILICON WAFER DURING PROCESSING.
Yaoqing Yang, Joonhyuk Kang, Jiang Yan, Ahmed Syed, Dim-Lee Kwong, and Guanghan Xu, Dept of Electrical and Computer Engineering, The University of Texas at Austin, TX.

Single wafer processing in the chamber becomes more popular nowadays. The main task during the processes is to keep the temperature uniform and to track the pre-described temperature trajectory. But first of all, we should measure and estimate the temperature profile precisely across a silicon wafer. Thus, accurate temperature measurement is a key factor to implement the rapid thermal processing (RTP). This paper presents a temperature estimation method using phase detection of acoustic wave and based on the frequency domain approach, our proposed technique increases the resolution of the temperature measurement and reduces the noise interference. In order to compare the performance, we obtained the parameter models of temperature distribution across a silicon wafer by optimization method using the thermocouple measurement data. Further more, these parameters may be used as feedback to control the heater array and achieve the desired results.

3:45 PM *I2.6
ION BEAM AND BIASED TARGET ION BEAM DEPOSITION TECHNIQUES FOR THE FABRICATION OF NON-VOLATILE MEMORY.
Joel A. Drewes, Honeywell, SSEC, Plymouth, MN; Harry Liu, Theodore Zhu, Honeywell, Inc.; Todd Hylton, Dave Baldwin, Boris Ciorneiu, CVC, Inc.

Ion beam deposition (IBD) is currently used to fabricate spin valves and magnetic bits for non-volatile memory. While existing IBD techniques are sufficient for research level applications and low level fabrication, a more suitable deposition technique will be required for commercial production of non-volatile memory products. One new method of deposition called Biased Target Ion Beam Deposition (BTIBD) appears to offer advantages over standard Ion Beam Deposition and Physical Vapor Deposition (PVD). The BTIBD methodology employs a low energy ion source and negatively biased target to generate a large plume sputtered flux. A second low energy source is directed at the substrate and may be used for cleaning or further film modification. Initial investigations of films produced with this technique suggest that it will provide a welcome addition to vapor deposition in the control of atomically engineered films and interfaces. Comparisons of BTIBD with IBD and PVD will be made for blanket films and patterned devices.

4:15 PM I2.7
THE DIFFICULTY OF GROWING SEMICONDUCTOR CONTINUOUS RANDOM NETWORKS BY VACUUM DEPOSITION.
J.M. Gibson, Argonne National Laboratory, Argonne, IL; M.M.J. Treacy, NEC Research Institute, Princeton, NJ; P.M. Voyles, Univ of Illinois, Dept of Physics, Urbana, IL and NEC Research Institute.

We have found, using a new experimental method (Fluctuation Electron Microscopy), that the as-deposited structure of amorphous silicon and germanium thin films is actually closer to a fine-grained polycrystalline structure. In an earlier paper [1], we postulated that the observed paracrystalline structure results from crystalline nucleation and accretion under conditions where the average grain size is less than the critically stable value of ~3 nm. In such cases, the film is observed to be unstable during thermal annealing, transforming into the continuous random network state. We have used molecular dynamics modeling to examine the atomistic characteristics of paracrystalline films. In this paper, we develop a simple thermodynamic model of the paracrystalline state that explains the observed instability. We discuss an extension of the model to describe nucleation and crystallization, and compare results with our experimental data. [1] J.M. Gibson, M.M.J. Treacy and P.J. Keblinski, *J. Non-Cryst. Solids*, **231**, 99 (1998).

4:30 PM I2.8
LOW PRESSURE PHOTO-ASSISTED MOCVD FOR THE PRODUCTION OF HOMOGENEOUS, LOW-STRAIN, AMORPHOUS TITANIUM OXIDE FILMS.
Peter Haycock, Mark Lopez, John Auld, Ailsa Williamson, John Bull, Ted Williams, Keele Univ, School of Chemistry and Physics, Staffordshire, UNITED KINGDOM.

The aim of this study was to produce films of amorphous titanium oxide which were homogenous, essentially strain-free, extremely smooth, with a high optical refractive index and low optical loss.

Metal-organic chemical vapor deposition (MOCVD) is a well established technique for the fabrication of very pure, conformal films, allowing a high degree of control over their crystallography, microstructure and texture. The deposition of crystalline titania films by MOCVD is well documented. A variety of precursors have been used, at atmospheric and reduced pressure, with and without the use of an oxidant, by means of pyrolysis or enhanced decomposition methods. To produce amorphous, low-strain material, we have used process parameters at the opposite extreme from those optimal for rutile deposition. In order to understand the significance of various parameters we have carried out depositions at a range of temperatures and pressures, using a range of carrier gas mixtures. The precursor was titanium tetraiosopropoxide, introduced into the carrier gas stream by liquid injection and flash evaporation. A UV lamp was used to assist many of the depositions. A clear trend was observed in that at higher temperatures the films were polycrystalline, with a very granular microstructure. Below 623 K the deposition mode appeared to change gradually from island growth to layer-by-layer deposition, with a reduction in crystallinity, increase in grain size and improved surface smoothness. The optimum process parameters included an Ar/N_2O carrier gas, a substrate temperature of 473 K and a reactor cell pressure of 5.6 torr, under UV radiation. This combination led to production of films which were amorphous, exhibiting a very fine grained, uniform microstructure with features of dimension around 15 nm, a complex refractive index of $2.54 + 5x10^{-4}i$, a titanium to oxygen ratio very close to 2:1 and a mean point-to-point roughness of around 1 $\AA$.

4:45 PM I2.9
DIAMOND SYNTHESIS WITH COMPLETELY CLOSED EACVD METHOD. Takashi Kato, Masahiro Nishida, Yoshiki Takagi, Teikyo Univ of Science & Technology, Yamanashi, JAPAN.

Many experimental results were reported of CVD diamond synthesis with so called flow systems, which need introduction of source gas and evacuation of reactant gas. For few years, we had been concentrated of developing completely closed diamond synthesizing system aimed for microgravity experiments. Recently we stared the new method with graphite as carbon source. With this method, completely closed system is successfully performed. Graphite rods are used as solid carbon source and at the same time as holder for activate hydrogen gas to hydrogen radicals. Silicon (100) wafer were used for substrates. Hydrogen gas was introduced into the reaction chamber with the suitable initial pressure, and controlled with Joule heating. The deposits were identified with SEM and Raman spectrometry. We tried to synthesize diamond on Si substrate under the conditions of forward bias where the substrate is held at a positive potential relative to the graphite rod. And also we tried the experiment under the reverse bias. We tried three different experiments, with forward, with reverse and without DC-bias. Typical DC-voltage was 100V. With DC-bias both positive and negative charge, synthesized diamond particles were getting large and coverage was wider than without DC-bias. Compared the reverse bias method with forward bias method, particle size for the former was about 0.7 micrometer, and for the latter was about 1 micrometer. Only for the reverse bias condition, single crystal particles with 5 micrometer in diamond were observed. With these experimental results, we will propose the model for synthesizing mechanism under the DC-bias conditions.

SESSION I3: MECHANISMS OF VAPOR DEPOSITION I

Chairs: William Barker and Robert L. Kosut
Tuesday Morning, April 25, 2000
Golden Gate A3 (Marriott)

8:30 AM *I3.1
NEW TECHNIQUES FOR DETAILED MEASUREMENT AND FUNDAMENTAL UNDERSTANDING OF POLYCRYSTALLINE THIN FILMS. R. Hull, D.N. Dunn and M.J. Williamson, Department of Materials Science, University of Virginia, VA; F.M. Ross, M. Reuter and R.M. Tromp, IBM Yorktown Heights Research Center, New York, NY; S.K. Kodambaka, I.G. Petrov and J.E Greene, University of Illinois, IL.

The microstructural evolution of polycrystalline thin films is extraordinarily complex. In this paper, we present new techniques for detailed characterization of polycrystalline Ti and TiN films grown on SiO_x substrates. These films are grown by ion-enhanced physical vapor deposition, and by a unique in-situ deposition system in an ultra-high vacuum transmission electron microscope (UHV-TEM). A complete description of the microstructural development of these systems is daunting. Nucleation densities are in the range 10e10 - 10e12 / cm^2. Nuclei will have varying orientations, growth rates and defect microstructures. When growth proceeds to the point of nuclei coalescence, subsequent growth of compound nuclei will be functions of relative nuclei orientations and sizes. Finally, when a continuous film is achieved, the final microstructure will be determined by many parallel and/or competing mechanisms, including competitive grain growth, defect generation mechanisms, and grain boundary grooving. To fully characterize these processes, techniques are required which can both track the evolution of individual nuclei with ultra-high (i.e. sub nm) spatial resolution, and can provide statistical analyses of large ensembles of particles. The ability to establish three-dimensional microstructural correlations is also critical. In this talk, we will describe novel electron- and ion-beam based techniques that can fulfill these requirements. Real-time evolution of individual nuclei, from nucleation through to film coalescence is studied using in-situ imaging of growth in a UHV-TEM. Statistical analysis of grain orientations and sizes with spatial resolution of order nms, and parallel analysis of thousands of grains is achieved using novel annular filtering techniques in the diffraction plane of a TEM. Finally, three-dimensional correlations are determined using a focused ion beam tomographic reconstruction technique. In combination, these techniques enable detailed measurement and understanding of the evolution of polycrystalline films. This work is supported by the DARPA-NSF Virtual Integrated Protoyping Program, and by IBM through an Academic Partner Award.

9:00 AM *I3.2
Stuart Parkin, IBM Almaden Research Center, San Jose, CA.

ABSTRACT NOT AVAILABLE

9:30 AM I3.3
KINETIC MONTE CARLO SIMULATION OF DYNAMIC PHENOMENA IN THIN FILM GROWTH. Martha A. Gallivan, David G. Goodwin and Richard M. Murray, Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA.

The ability to dynamically sense and control process conditions during thin film growth opens up the possibility of using transient processing for microstructural control. Motivated by our interest in epitaxial $YBa_2Cu_3O_{7-x}$ films, which typically grow via spirals centered on screw dislocations, in this study we use a kinetic Monte Carlo model to explore how the competition between spiral growth and two-dimensional island nucleation may be altered dynamically. The results show that sinusoidal modulation of the temperature and precursor flux can result in a transition from spiral growth to growth via two-dimensional island nucleation, under appropriate conditions. The modulation frequency, amplitude, and relative phase between temperature and flux have been investigated, and are all important. Relatively simple modulation techniques should be able to provide a significant degree of microstructural control during growth. Experiments are now underway to validate and test these model predictions.

10:15 AM I3.4
A DRASTIC CHANGE IN STRUCTURE AND PROPERTY OF TiO_2 THIN FILMS DEPOSITED BY METAL-ORGANIC CHEMICAL VAPOR DEPOSITION WITH DEPOSITION TEMPERATURE. Jeong-Hoon Park, Kug-Sun Hong, School of Materials Science and Engineering, Seoul National University, Seoul, KOREA; Woon-Jo Cho, Photonics Research Center, Korea Institute of Science and Technology, Seoul, KOREA.

TiO_2 thin films were deposited by metal-organic chemical vapor deposition (MOCVD) method using alkoxide source, titanium tetraisopropoxide (TTIP) at working pressure, 0.6 Torr. The variation in the structure and physical property of the film with the varying deposition condition was investigated through various characterization tools. A drastic change in structural aspect and its property occurred when the deposition temperature increased above 400°C From X-ray diffraction (XRD), it was observed that the crystallinity and the degree of texturing was decreased significantly around 400°C. The surface microstructure has changed explicitly from continuous and smooth one to rough one above this deposition temperature, which is demonstrated from the scanning electron microscopy (SEM). Bright field image of transmission electron microscopy (TEM) verified the abrupt microstructural change of considerable decrease in grain size by about one third to one fifth and the appearance of significantly channeled pore along the grain boundary. Deposition kinetics was proved to transit from reaction controlled regime into diffusion controlled regime above about 400°C in Arrehnius plot, which is suggested as the mechanism that bring about the explicit micro-structural change described above. A lot of physical properties have also changed above 400°C. Electrical resistivity of the films surged from about 10Ω·cm to about $10^3\Omega$·cm, which is measured by the 4-point probe method. While UV-vis transmission spectra of the films deposited on alumino silicate glass showed that the transmittance maxima curves increased slightly above the temperature, the refractive index calculated by envelope method has significantly

decreased from 2.45 to 2.25 at 630nm. What was measured by ellipsometer for the films deposited on Si single crystal wafer has changed similarly. Infrared reflectance spectra demonstrated that a band near 450cm^{-1} assigned as O-Ti-O vibration was highly reduced in intensity, which confirmed again the decrease of crystallinity observed in XRD. Judged by the changes in these physical properties, the porous microstructure of films deposited at above 400°C was thought to be responsible for the significant decrease in electrical conductivity and refractive index of the films.

10:30 AM I3.5
ORIENTED CRYSTALLIZATION OF GaSb ON PATTERNED Si SUBSTRATES. S.S. Yi, P.D. Moran, T.F. Kuech, Univ of Wisconsin-Madison, Dept of Chemical Engineering, Madison, WI; X. Zhang, F. Cerrina, Univ of Wisconsin-Madison, Dept of Electrical and Computer Engineering, Madison, WI; J. Carter, H.I. Smith, Massachusetts Inst of Tech, Dept of Electrical Engineering and Computer Science, Cambridge, MA.

Graphoepitaxy is a method of oriented crystallization of films on amorphous substrates. In contrast to the conventional heteroepitaxy, the oriented growth of crystalline films is induced by forming an array of appropriate relief patterns on amorphous substrates. We present the substrate-induced oriented crystallization of GaSb on amorphous Si surfaces. GaSb-based compound semiconductors are of great interest for infrared optoelectronic devices over the ranges from 1.24 μm for AlGaAsSb to 4.4 μm for GaInAsSb, and high-speed electronic devices. To accommodate octahedral growth shapes of GaSb crystallites, inverted square pyramids with {111} sidewalls are patterned on (100) Si substrates using x-ray lithography and anisotropic etching. The orientation and structure of GaSb crystals at various stages of the nucleation are examined by scanning electron microscopy and x-ray diffraction. In the early stage of growth, preferential nucleation of GaSb crystallites at the apexes and the corners of inverted square pyramids is clearly notable. As the growth proceeds, large-grained GaSb crystals grow out of inverted square pyramids. X-ray diffraction pole figure analysis shows evidence of sidewall texture of {111} planes. Extra (111) spots observed in a x-ray diffraction pole figure are interpreted in terms of multiple twinning of GaSb. The effects of growth temperature and the size of pattern on oriented crystallization are also investigated.

10:45 AM I3.6
THE EFFECTS OF ATOMIC HYDROGEN ON THE GROWTH OF EPITAXIAL AND POLYCRYSTALLINE GROUP IV THIN FILMS. Yongjun Zheng, Andrew M. Lam, Todd W. Schroeder, James R. Engstrom, Cornell University, School of Chemical Engineering, Ithaca, NY.

Supersonic molecular beam techniques have been used to study the kinetics of gas-source Group IV thin film deposition, focussing on the effects of coincident fluxes of atomic hydrogen on both the nucleation and growth regimes. For example, concerning nucleation, and the suppression thereof, the etching of Ge thin films (deposited on Si substrates) by atomic hydrogen has been examined using in situ x-ray photoelectron spectroscopy. Concerning (steady-state) growth, we have modeled data obtained by reflection high energy electron diffraction (RHEED) to understand the effects of atomic hydrogen on the epitaxial growth rate of Si, where Si_2H_6 is used as the source. Based on the knowledge gained from these and other studies, a novel process has been developed to achieve selective epitaxial growth (SEG) of Group IV thin films of arbitrarily large thickness using atomic hydrogen. Compared with methods that employ Cl-based processes/chemistry, this new process requires much lower thermal budget (process temperature < 650°C), which makes it very promising for potential applications in the semiconductor industry.

11:00 AM I3.7
OBSERVATION OF RHEED OSCILLATIONS DURING LOW TEMPERATURE GROWTH OF SILICON ON SILICON BY PULSED LASER DEPOSITION. Jamey S. Pelt, Rafael Magaña Jr., Matthew E. Ramsey, Edward Poindexter, Steven Atwell and Steven M. Durbin, Florida A&M University and The Florida State University, Department of Electrical Engineering, Tallahassee, FL.

Known for its wide-spread use in the fabrication of thin film high-temperature superconductors, pulsed laser deposition (PLD) is characterized by several somewhat unique features. In particular, the average kinetic energy of species within the vapor plume can lie within the range of 10 to 100 eV, compared to ~0.1 eV for thermal evaporation techniques. Also, time-average growth rates are typically comparable to other techniques, but the vapor species are delivered in short pulses with a duration on the order of 10 to 100 microseconds. As a result, the dynamics of film formation are rather different from other physical vapor deposition techniques. Recent theoretical studies have suggested that significantly smoother surface morphology may be attainable at low substrate temperatures using PLD, despite the rather short time that characterizes adatom incorporation. This paper presents the results of a study of homoepitaxial silicon growth by PLD using in-situ reflection high-energy electron diffraction and post-growth analysis by atomic force microscopy. A KrF laser was used to ablate a silicon target using a fluence of approximately 0.2 to 1 J/cm^2 and a pulse repetition rate of 1 to 5 Hz. The substrate temperature was varied from room temperature to 900°C. At low substrate temperatures, the RHEED intensity drops quickly, with an amorphous pattern eventually replacing the substrate diffraction pattern. For moderate substrate temperatures, the substrate pattern is observed to fade, eventually being replaced by a Debye-Scherrer ring pattern indicating growth of polycrystalline material. However, for temperatures greater than approximately 500°C, sustained RHEED intensity oscillations have been observed with a period of ~50 seconds which persist for over 10 minutes of film growth. At the end of the 30 minute film growth, a chevron-like RHEED pattern indicative of extreme surface roughness is observed. Atomic force microscopy characterization of the surface morphology is in progress.

11:15 AM I3.8
IN-SITU CHARACTERIZATION OF GaN GROWTH MODES USING X-RAY SCATTERING. A. Munkholm, G.B. Stephenson, M.V. Ramana Murty, J.A. Eastman, O. Auciello, Argonne National Laboratory; C. Thompson, Northern Illinois University and Argonne National Laboratory; P. Fini, R. Jothilingam, S.P. DenBaars, J.S. Speck, University of California, Santa Barbara, CA.

GaN-based materials for device fabrication utilize film growth by metal-organic chemical vapor deposition (MOCVD). Using synchrotron x-ray scattering, which is compatible with this reactive vapor phase environment, we have performed *in-situ* measurements of the atomic-scale surface structure and morphology of GaN during growth. By real-time monitoring of the crystal truncation rod intensity, we can determine the growth rates and growth modes. We have observed 3D, layer-by-layer and step-flow growth modes and determined the process conditions at which the growth mode transitions occur. In some cases, we observe a direct transition from step-flow to 3D growth without an intervening layer-by-layer mode. The temperature and ammonia partial pressure dependence of the surface structure is consistent with a simple model of the equilibrium between the vapor phase and the surface coverage of Ga and N. We have obtained information on the surface kinetics both from the recovery time constants following growth and from the temperature and growth rate dependence of the growth mode transitions. Effects on growth behavior after dosing with silicon will also be discussed.

11:30 AM I3.9
MORPHOLOGICAL, CHEMICAL AND STRUCTURAL STUDY OF SPUTTERED NANOLAMINATED Al/Al_2O_3 THIN FILM COMPOSITES. Claire Le Paven-Thivet, Pascal Aubert, Charlotte Malibert, Fayal Sadi, Philippe Houdy, Dèpartement Sciences des Matèriaux, Universitè Evry-Val d'Essonne, FRANCE; Stèphane Fusil, Alain Zozime, Lab. Phys. des Solides de Bellevue, Meudon, FRANCE.

For application in the field of hard and wear resistant coatings, nanolaminated Al/Al_2O_3 thin film composites were deposited by reactive sputtering, at different substrate temperatures (Ts). This study focuses on the influence of the morphological, chemical and structural characteristics of individual Al and Al_2O_3 films on the behaviour of Al/Al_2O_3 composites. The morphological study was conducted by High Resolution Scanning Electronic Microscopy (HR-SEM) and Atomic Force Microscopy (AFM). Cross-section HR-SEM observations were performed on composites. Chemical composition and chemical diffusion were determined by Wavelength Dispersive Spectrometry (WDS) and High Resolution Secondary Ion Mass Spectrometry (HR-SIMS). Crystalline properties were investigated by X-Ray Diffraction (XRD), whereas X-Ray Reflectometry was used to obtain thickness and roughness of layers. The growth of aluminium is clearly tridimensional, on very thin films (namely 10-15 nm thick) and thin films (300 nm thick). The Root Mean Square roughness is about 10% of the total thickness in both films. This high value undoubtedly prevents the formation of morphological abrupt interfaces between Al and Al_2O_3, the latter having very smooth surfaces. Better behaviour of Al films is obtained when deposition is performed at low substrate temperature, in correlation with the appearance of a quenched growth at the cryogenic temperature Ts = - 90°C. The existence of multilayers in Al/Al_2O_3 composites was proved by HR-SIMS with the appearance of a periodic signal. XRR experimental patterns have also shown several Bragg peaks, which is the signature of a periodic structure. These results have been confirmed by preliminary TEM analysis. In addition, the multilayering character of Al/Al_2O_3 increases when Ts decreases, in good accordance with the decreasing of aluminium grain size. An explanation of the formation of interfaces and growth of multilayers in Al/Al_2O_3 will be finally presented.

11:45 AM I3.10
DEVELOPMENT OF RESIDUAL STRESS IN SPUTTER DEPOSITED METAL HYDRIDE THIN FILMS. David P. Adams, Juan Romero, Jerry Floro, Ronald Goeke and Jim Banks, Sandia National Laboratories, Albuquerque, NM.

This work investigates the growth of metal hydride thin films by reactive sputter deposition. Metal hydride thin films are currently of interest for miniature fuel cells as well as switchable mirrors. In particular, stoichiometric metal hydride phases which have hydrogen as its main constituent are desired for these various applications. In the present study, the development of metal hydride thin film residual stress and microstructure is explored as a function of the growth parameters. By controllably varying the growth temperature and the metal/hydrogen arrival rates, we are able to lock in different desired phases. This includes deposition of rare-earth metal - hydrogen compounds such as erbium dihydride and erbium trihydride; phase analysis involves Rutherford backscattering spectrometry, forward recoil spectroscopy and x-ray diffraction. The residual stress of metal hydride films is investigated in order to establish techniques for tailoring / controlling this property. A multi-beam wafer curvature sensor is used for in-situ, real time analysis of residual stress. Thin film microstructure is investigated using x-ray diffraction and electron microscopy in order to determine the origin of residual stress. This study includes an examination of crystal texture. This work was performed at Sandia National Laboratories and is supported by the United States Department of Energy under Contract No. DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

SESSION I4: MECHANISMS OF VAPOR DEPOSITION II

Chairs: John C. Bean and David J. Srolovitz
Tuesday Afternoon, April 25, 2000
Golden Gate A3 (Marriott)

1:30 PM *I4.1
THRESHOLD PHOTOEMISSION AS AN IN-SITU DIAGNOSTIC OF THIN FILM QUALITY. J.J. Zinck, R. Ross, HRL Laboratories, LLC, Malibu, CA; W.J. Barvosa-Carter, J.H.G. Owen, C. Ratsch, UCLA, Dept. of Mathematics, Los Angeles, CA.

Threshold photoemission (PE) is a versatile tool to examine many different features of thin film growth. This technique can compliment and in some cases replace the use of more conventional techniques, such as RHEED and mass spectrometry. Due to the inherent sensitivity to both the chemical nature of the surface and its morphology, signatures from PE can be used to monitor such processes as oxide desorption, reconstruction changes, alloy composition, surface segregation, and developing surface roughness. This paper describes the application of threshold photoemission in the optimization and control of the interface morphology in quantum strucutures containing the 6.1 $\AA$ materials InAs, AlSb, and GaSb. The features associated with PE will be discussed in reference to simultaneous RHEED and mass spectrometry data and correlated with in situ full wafer scanning tunneling microscopy. Ab initio calculations, which have been used to identify specific contributions of surface species to the photoemission signature, will also be discussed.

2:00 PM *I4.2
ATOMIC LAYER DEPOSITION OF THIN FILMS USING SEQUENTIAL SURFACE REACTIONS. Steven M. George, Dept. of Chemistry, University of Colorado, Boulder, CO.

Thin films can be deposited with atomic layer control using sequential surface reactions. This talk will describe the deposition of compound and single-element films using the appropriate surface chemistry. The deposition of dielectric Al_2O_3 films and conducting tungsten films will be used as examples to illustrate the generic approach.

3:00 PM I4.3
HIGH ENERGY ION IMPACT EFFECTS DURING MULTILAYER DEPOSITION. X.W. Zhou, David Zou and H.N.G. Wadley, Department of Materials Science and Engineering, School of Engineering and Applied Science, University of Virginia, Charlottesville, VA.

Many new technologies rely on vapor deposited thin film multilayers. For instance, a new generation of non-volatile memory devices are built from giant magnetoresistive material, which is either metallic multilayers composed of Co/Cu/Co thin layers or magnetic tunnel junction multilayers composed of Co/AlxOy/Co thin layers. In these multilayer structures, it is necessary to minimize the atomic scale interfacial roughness and interlayer chemical mixing. During rf diode sputtering, ions with energies between 50 and 200 eV can impact a growth surface. Molecular dynamics method has been used to study the effects of high energy Ar+ and Xe+ ion impact on the surface roughness and interlayer mixing of a model nickel on copper surface. The results indicated that high energy (50 - 200 eV) ion impacts induce pits and surface roughness by ejecting surface atoms on to the top of the surface. Impacts of ions with energy above 50 eV also cause mixing due to the exchange of a surface nickel atom with a copper atom in the underlying crystal. The extent of the mixing increases with ion energy, but decreases as the number of the nickel monolayers above the copper crystal increases. While Xe+ and Ar+ ions have a similar mixing effect at low ion energies ($\sim$50 eV), Xe+ induces more significant mixing at an ion energy of about 200 eV.

3:15 PM I4.4
NANOSTRUCTURE FORMATION BY ION EROSION. M.V. Ramana Murty[a], A.J. Couture[b] and B.H. Cooper[b]. [a]Materials Science Division, Argonne National Laboratory, Argonne, IL, [b]Department of Physics and Cornell Center for Materials Research, Ithaca, NY.

Erosion of a crystalline material with energetic ions often leads to a "patterned" surface with nanometer scale feature size and separations. The features may be mounds, pits, or both. For most applications it is important to be able to control the shape of the nanoscale features in addition to their regular arrangement. For example, isolated regularly arranged mounds can serve as an array of quantum dots whereas a surface with regularly arranged pits can serve as a template for a different material to be deposited. Using kinetic Monte Carlo simulations, we have identified that the ratio of adatom yield (Y_a) to sputter yield (Y_s) plays a key role in the evolution of surface morphology. At a given (intermediate) temperature, a high Y_a/Y_s ratio leads to a surface predominantly covered with mounds whereas a low Y_a/Y_s ratio favors pits. Independent of the Y_a/Y_s ratio, we observe a transition from a surface covered with mounds to a surface covered with pits with increasing temperature. We will discuss how one may experimentally control the Y_a/Y_s ratio and illustrate with STM images of ion eroded Au(111). This work was supported by the US DOE, BES–DMS under contract W-31-109-ENG-38 and the Cornell Center for Materials Research funded by NSF under DMR–9632275

3:30 PM I4.5
SURFACE AND BULK STRUCTURES IN DIAMOND CVD: IMPLICATIONS ON GROWTH MECHANISMS AND MULTISCALE MODELING. J.E. Butler, Naval Research Laboratory, Washington, DC; C.C. Battaile, Sandia National Laboratory, Albuquerque, NM; D.J. Srolovitz, Princeton Materials Institute, Princeton University, Princeton, NJ; D.S. Dandy, Colorado State University, Fort Collins, CO; S.J. Harris, Chemistry Department, Ford Scientific Research Labs, Dearborn, MI; J.W. Steeds, Department of Physics, University of Bristol, Bristol, UNITED KINGDOM; I.I. Oleinik, D.G. Pettifor and A.P. Sutton, Department of Materials, Oxford Univ., Oxford, UNITED KINGDOM.

Surface and bulk morphologies of single crystal and polycrystalline chemical vapor deposition (CVD) diamond have been examined using scanning electron, scanning probe, and transmission electron microscopies. Both doped and undoped samples have been examined. The morphologies and defects observed provide both insights, challenges, and constraints for the development of multiscale modeling approaches for complex chemical vapor deposition processes.

3:45 PM I4.6
ION-BEAM TEXTURING MECHANISMS BY OBLIQUE ION BEAMS IMPINGING ON METAL OXIDES. Paul Berdahl, Ronald P. Reade, Lawrence Berkeley National Laboratory, Berkeley, CA.

During Ion Beam Assisted Deposition (IBAD) an oblique ion flux is directed at the surface of a metal oxide film such as yttria stabilized zirconia (YSZ). In this case fully oriented crystallite formation is promoted by argon ion energy near 300 eV and ion angle near 55 deg. Elevated temperature is helpful in promoting formation of crystalline rather than amorphous phases, and for annealing of defects, but in some cases elevated temperature causes (111) rather than the desired (001) fiber texture. Due to preferential sputtering of oxygen, ambient oxygen is required to maintain stoichiometry. Recent work by us and other groups on other oxides such as CeO_2 and MgO will be discussed with an eye toward identifying common and distinguishing features. Despite considerable experimental and theoretical work, the mechanism of texture formation is still controversial. It is agreed that the ion penetration distance is only a few atomic layers and that the ion direction interacts with crystallite orientation. Also, it is known that the presence of the free surface is required for complete crystallite orientation. Further, it appears that unwanted polycrystalline texture requires a lengthy period of competitive grain growth to correct. Thus, amorphous substrates are desirable. Controversial aspects of texture

formation include: What is the role of sputtering? Is short-range ion channeling a useful qualitative picture? Are mechanisms different in oxides vs. metals? In situ RHEED patterns will be used to provide data to further clarify the experimental situation.

4:00 PM I4.7
CORRELATION OF SURFACE STRUCTURE EVOLUTION AND GROWTH MECHANISMS IN POLYCRYSTALLINE FILMS.
Adriana E. Lita and John E. Sanchez, Jr., Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI.

There is significant interest in understanding the mechanisms that control the structure of vapor deposited films due to their wide applications as critical components in electronic, magnetic and optical devices. An improved understanding may be achieved through combined characterization of surface structure and underlying microstructure during film growth. Therefore, we have examined the evolution of surface structure and microstructure of Al and Al-0.5wt.% Cu polycrystalline thin films at different deposition conditions. Atomic force microscopy and subsequent dynamic scaling analysis were used for studying the surface structure evolution. Film microstructure (grain size and crystallographic texture) was determined by transmission electron microscopy and x-ray diffraction pole figure analysis. We have correlated surface structure evolution and theoretical scaling results with the mechanisms that drive microstructure evolution. We found that the physical processes acting on length scales smaller than the median grain size can be identified based on growth mode theories developed for single crystal surface evolution. At larger length scales grain effects must be included in order to understand the film growth mechanisms. Consequently, grain growth accomplished through grain boundary movement has been identified as an important mechanism that affects surface structure as well as grain size and crystallographic texture. The grain growth mechanism is strongly dependent on film deposition conditions. For example, Al-0.5wt.% Cu films deposited on Ti underlayer developed a perfect (111) texture, whereas films deposited on SiO_2 underlayer developed a near- (111) texture, larger average grain size and rougher surfaces throughout film evolution. In order to single out the grain effects on surface structure of polycrystalline films, a comparison between dynamic surface scaling of Al polycrystalline versus epitaxial films will be discussed.

4:15 PM I4.8
REAL TIME, IN SITU CURVATURE MEASUREMENT DURING GROWTH OF EPITAXIAL YBCO FILMS ON MGO. D.A. Boyd, M.A. Gallivan, A.B. Tripathi, A.J. Rosakis, D.G. Goodwin, H.A. Atwater, Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA.

We have implemented coherent gradient sensing (CGS) to measure, in situ, the initial substrate curvature and changes in curvature induced by MOCVD growth of thin film YBCO on 0.5 x 50 mm MgO (001) substrates. CGS is a novel, real-time, full-field optical technique that provides a direct map of the components of the curvature tensor across the entire surface of the wafer. A well-characterized 700 nm thick YBCO film on a on 25 x 25 x 0.5 mm MgO substrate was monitored with CGS as the temperature was increased from 25 to 1000°C. The curvature was found to be spatially nonuniform and changes in curvature during heating were observed in real time. By Stoney's equation, the observed curvature could be related to the thermal mismatch of the film and substrate, resulting in values above 0.4 GPa in both directions. Further, the tetragonal to orthorhombic phase transformation YBCO exhibits upon cooling back to room temperature in oxygen could be detected with CGS, via the curvature change due to the local changes in stress resulting from the phase transition.

4:30 PM I4.9
NEW IN-SITU SENSING TOOL FOR MONITORING THIN FILM GROWTH VIA HEAT CAPACITY MEASUREMENTS: SCANNING NANOCALORIMETRY. M. Efremov, M. Zhang, F. Schiettekatte, E. Olson, A. Kwan, S.L. Lai and L.H. Allen, Materials Science Department, University of Illinois at Urbana, Urbana, IL.

We introduce a novel in-situ technique for monitoring thin film growth via heat capacity measurements using a new ultra sensitive instrument - Differential Scanning Nanocalorimeter [1-3]. The new probe is sensitive to the deposition of less than1 angstrom of material [4] and can be used to monitor the process of growth during deposition. This is especially important in the first 20 angstrom of growth during which island formation occurs and the heat capacity properties of the material changes dramatically due to melting point depression of the small islands. In this paper we present data on the growth of In and Sn on a Si-N surface during physical vapor deposition. We use the nanocalorimeter to perform temperature scans from ambient through the melting point of each material. The data show the successive states of the thin film at the discontinuous stage of growth. There is an extremely broad range of melting temperatures (>70 degrees C) for the island ensemble at the beginning of the deposition indicating a large variation of island size. Whereas the data for thicker more continuos film shows an extremely narrow (<5 degrees C) range of melting temperatures. The melting point depression phenomenon and the difference in the behavior of these two metal films during the early growth stage will be discussed.
Reference:
1. S.L. Lai, J.Y. Guo, V. Petrova, G. Ramanath, and L.H. Allen, Phys. Rev. Lett., 77 (1996) 99.
2. S.-L. Lai, P. Infante and L.H. Allen, Appl. Phys. Lett., 70, 43-46 (1997)
3. S.L. Lai, J. Carlsson and L.H. Allen, Appl. Phys. Lett. 72, 1098 (1998)
4. M. Efremov, M. Zhang, F. Schiettekatte, E. Olson, A. Kwan S.L. Lai and L.H. Allen, To be submitted to Appl. Phys. Lett. (1999)

4:45 PM I4.10
KINETIC ROUGHENING DURING Xe HOMOEPITAXY: AN OPTICAL REFLECTIVITY DIFFERENCE STUDY. Edward Nabighian, X.D. Zhu, University of California at Davis, Dept. of Physics, Davis, CA; Maria C. Bartelt, Sandia National Laboratories, Livermore, CA.

Homoepitaxy provides simple systems on which one can test recently developed ideas on film growth far from equilibrium. Rare-gas homoepitaxy has an additional advantage since the interactions between adatoms are known. We studied the growth of Xe films on Ni(111), between 35 and 60K, using an optical reflectivity difference technique. The mean Ni terrace width was almost 100 nm. Deposition rates were in the range of 0.002ML/s at a Xe pressure of 3.3×10^{-8} Torr. Previous LEED studies of this system [1] revealed a commensurate $\sqrt{3} \times \sqrt{3}$R30° structure in the first Xe layer with saturation coverage of ~1/3. Thus, the first layer of Xe is compressed by only 1.4%, and subsequent multilayer growth proceeds on a nearly stress-free Xe(111) substrate. We observed rough growth below 37K, and a transition to near layer-by-layer growth around 40K where oscillations in the reflectivity difference persist for many layers. Desorption-induced roughening is observed above 60K. The transition to layer-by-layer growth is characterized in terms of a critical island radius, R, for second layer nucleation, whose dependence on system parameters and deposition conditions is examined using kinetic Monte Carlo simulations. At low temperatures, rough growth reflects a small R, compared to the mean island radius, due to significant additional step-edge barriers. For Xe/Xe(111), these are between 20 and 25meV, smaller near kink sites. (The barrier for terrace diffusion is only ~8meV.) Kink densities reflect barriers for diffusion at island edges (~40meV for A-type, and ~20meV for B-type), and around island corners (~50meV), and the strength of Xe-Xe adatom bonds (~20meV for a dimer). Simulation results also point to the possibility that minute concentrations of impurities or defects in the Xe layers stabilize island formation during growth at higher temperatures. MCB is supported by the USDOE-BES under contract #DE-AC04-94AL-85000. [1] A. Wong and X.D. Zhu, Appl. Phys. A 63 (1996) 1.

SESSION I5: MODELS OF VAPOR DEPOSITION I
Chairs: George H. Gilmer and Robert Hull
Wednesday Morning, April 26, 2000
Golden Gate A3 (Marriott)

8:30 AM *I5.1
ATOMISTIC INPUT TO SIMULATIONS OF MICROSTRUCTURE, MORPHOLOGY AND TEXTURE EVOLUTION IN FILM GROWTH. D.J. Srolovitz, Princeton Materials Institute, Princeton University, Princeton, NJ.

The evolution of polycrystalline film microstructure, morphology and texture during vapor phase growth is ultimately determined by the normal velocity of the growth front (we neglect grain boundary migration here). This velocity is determined by such factors as the rate of surface chemical reactions in CVD, the rate of sputtering from the growing surface in ion beam assisted deposition (BAD), and shadowing effects. We employ atomistic simulations (i.e., first principles calculations, molecular dynamics and kinetic Monte Carlo methods) to determine the rate of growth of single crystal films of different orientation under a variety of growth conditions. We explicitly examine the cases of the CVD of diamond, PVD of MgO and IBAD of Al. We then use these atomistic results to examine the evolution of the film on a microstructural scale using both front tracking methods in 2-d and level set methods in 3-d. I will show several qualitative examples of microstructure and morphology evolution using both methods, as well as quantitative comparisons with experiments (grain size, texture, etc.)

9:00 AM *I5.2
THE ROLE OF COMPUTATIONAL MODELS IN DESIGNING TRANSIENT OPTIMAL-CONTROL STRATEGIES FOR THIN-FILM PROCESSING. Robert J. Kee, Laxminarayan L. Raja, and Tyrone L. Vincent, Division of Engineering, Colorado School of Mines, Golden, CO.

There are potentially some very great benefits to developing materials processes that deliberately vary process conditions, like pressure, temperature, or flow rates, during the course of the process. Today, by contrast, nearly all thin-film processing is done under steady-state conditions. Full transient processing holds the promise of reducing manufacturing cost and the possibility of producing material systems that would be infeasible to manufacture with steady processes. Among the applications that can benefit from transient processing are multi-layer structures, with precise functional requirements for the interfaces of transitions between layers. Such requirements are driven by electrical, optical, magnetic, or mechanical properties. Once the notion of transient processing is embraced, there is a need and opportunity to develop optimal trajectories through which the process will proceed. The optimization algorithm seeks to minimize a general representation of process cost, while respecting imposed constraints. Physically based models that represent the fluid-flow, thermal transport, and process chemistry can provide critical elements in understanding processing alternatives. Equally important, however, is the development of computational tools that can be used to manipulate the physical models in ways that identify optimal processing strategies. In this presentation, we discuss optimization algorithms and software that identify minimal-cost processing paths. Once an optimal process trajectory is identified, there is a need to design process-control strategies to implement the trajectory. Again, computational algorithms that manipulate physical models are important tools in the concurrent design of processes and processing equipment. This presentation draws on examples from the metal-organic chemical vapor deposition of yttrium-barium-copper-oxide, thin-film, superconductors. The physical models consider the chemically reacting process flows as well as the radiative and conductive heat transport in the reactor assembly. The optimization and control algorithms are developed in a very general setting, which can be applied to a wide range of other processes.

10:00 AM *I5.3
MULTISCALE MODELS OF VAPOR PHASE DEPOSITION PROCESSES. Klavs F. Jensen, Raj Venkataramani, Seth T. Rodgers, Gwang S. Kim, and Maria Nemirovskaya, Massachusetts Institute of Technology, Department of Chemical Engineering, Cambridge, MA.

The need to understand the relationship between processing and device performance for vapor phase deposition processes is driving the coupling of molecular level simulations with traditional macroscopic transport phenomena descriptions. The development of predictive, efficient models that bridge across multiple length and time scales raises new challenges in terms of simulation strategies, numerical algorithms, and experimental validation. These are exemplified through studies linking quantum chemistry, molecular dynamics (MD), kinetic Monte Carlo (MC), and macroscopic finite element simulations. Process examples are drawn from chemical and physical vapor deposition of metals as well organometallic chemical vapor deposition (OMCVD) of III-V compound semiconductors. Specifically, experimental observations and quantum chemistry predictions of elementary surface reactions are incorporated into MD and MC simulations to provide new understanding of microstructure evolution. By flux balances and level set methods, the results of these computations are subsequently incorporated into self-consistent feature and reactor scale models. Comparisons with experimental data are given at each length scale along with a discussion of the type of data needed to validate multiscale models.

10:30 AM I5.4
DIAMOND CVD GROWTH MECHANISMS AND REACTION RATES FROM FIRST-PRINCIPLES. I.I. Oleinik, A.P. Sutton and D.G. Pettifor, Oxford University, Department of Materials, Oxford, UNITED KINGDOM; C.C. Battaile, Sandia National Laboratories, Albuquerque, NM; D.J. Srolovitz, Princeton University, Princeton, NJ; J.E. Butler, Naval Research Laboratory, Washington, DC; D.S. Dandy, Colorado State University, Fort Collins, CO; M.P. D'Evelyn, GE Corporate Research and Development, Schenectady, NY; S.J. Harris, Ford Scientific Research Laboratory, Deaborn, MI.

CVD diamond is an enabling material for diverse applications. In recent years, multiscale modelling of CVD growth in conjunction with experimental studies of the deposition processes has made a substantial progress towards our understanding of the fundamental growth chemistry and material quality. Macroscopic gas phase simulations of the CVD reactor, the mesoscale kinetic Monte-Carlo modelling of the crystal growth and nanoscale modelling of the surface chemistry are three main legs in the multiscale hierarchy. In the framework of this methodology we have performed first-principles quantum mechanical calculations of bonding and reaction kinetics of the elementary growth processes and provided critical input in the form of atomistic growth mechanisms and reaction rates for the mesoscale KMC modelling of CVD diamond growth. A key success was achieved by combining first-principles and Monte Carlo studies to elucidate (100) growth mechanisms that have perplexed the diamond growth community for many years.

10:45 AM I5.5
ATOMIC-SCALE MODELING OF THIN METALLIC FILMS DEPOSITED BY SPUTTERING FOR Si DEVICE INTERCONNECTS. J. Dalla Torre[1,2], G.H. Gilmer[1], D.L. Windt[1], F.H. Baumann[1], R. Kalyanaraman[3], M. Djafari Rouhani[2]. [1]Bell Labs, Lucent Technologies, Murray Hill, NJ, [2]LAAS-CNRS & LPST-ESA5477 CNRS, Universite Paul Sabatier, Toulouse, FRANCE, [3]Oak Ridge National Labs, Oak Ridge, TN.

We present atomic scale simulations of metal films deposited by sputtering. We are interested in the structure of films deposited onto non-planar (i.e. inclined) surfaces, as in deep submicron trenches and vias used in microelectronics, and in the mechanisms involved in the growth of low mobility materials (e.g. Ti, Ta, TiN etc.). Our Monte Carlo model (ADEPT) includes ballistic deposition from a sputter target, surface diffusion, and allows multiple orientations corresponding to polycrystalline material. The effect of the kinetic energy of the impinging atoms on the growing film is included using a binary collision model. Deposition angle, texture, reduced mobility, grain boundaries all influence the morphology, the microstructure, the density and the roughness of the growing layer. Other effects can dominate the growth: imperfect wetting between the film and the substrate causes the formation of clusters. These clusters can initiate columnar growth, with the result that sections of the substrate are not covered by the film. High adatom diffusivity on the substrate produces widely spaced and large clusters, and if they merge, a polycrystalline film composed of large grains is produced. On the contrary, low adatom diffusivity on the substrate leads to a high density of clusters and a fine polycrystalline structure. The deposited film covers the substrate completely. In addition, the Ehrlich-Schwoebel barrier yields a growth instability that can also initiate columnar structure. The kinetic energy of the deposited atoms and of reflected Ar atoms is shown to modify the film morphology by resputtering and biased diffusion mechanism. Here, we discuss some of the effects that are significant in Cu, Al, Ti and Ta thin films. Finally, we discuss experimental results, including X-Ray reflectance measurements, HRTEM images in the light of these simulations.

11:00 AM I5.6
KINETIC LATTICE MONTE CARLO SIMULATION OF POLYCRYSTALLINE THIN FILM GROWTH. Zhiyong Wang, Science and Engineering of Materials Program, Arizona State University, Tempe, AZ; James B. Adams, Department of Chemical, Bio and Materials Engineering, Arizona State University, Tempe, AZ.

We present a three-dimensional Kinetic Lattice Monte Carlo (KLMC) model which is capable of simulating polycrystalline thin film growth including multiple grain orientations for large spatial scales for long times. Our first application of this code is to the growth of Mo tips typically deposited by physical vapor deposition (PVD) and used for field emission display emitters. Some important results, such as the crystal orientation, the grain shape, the grain size, and the sharpness of Mo tips as a function of the processing conditions, including deposition rate, substrate temperature, annealing temperature, and annealing time, will be presented.

11:15 AM I5.7
KINETIC MONTE CARLO SIMULATIONS OF ETCHING DURING DIAMOND CHEMICAL VAPOR DEPOSITION. C.C. Battaile, Sandia National Laboratories, Albuquerque, NM; D.J. Srolovitz, Princeton University, Princeton, NJ; I.I. Oleinik, D.G. Pettifor and A.P. Sutton, Oxford University, Oxford, UNITED KINGDOM; J.E. Butler, Naval Research Laboratory, Washington, DC; S.J. Harris, Ford Scientific Research Laboratory, Dearborn, MI; D.S. Dandy, Colorado State University, Fort Collins, CO.

Thin polycrystalline diamond films with outstanding mechanical, thermal, optical, and electronic properties can be fabricated by chemical vapor deposition. Much of our knowledge about molecular diamond formation mechanisms is derived from combustion data and atomistic calculations. However, current theories of diamond growth, while successful in reproducing some of the features of diamond deposition, are in stark qualitative contrast with several well-established observables. In particular, measurements of facet growth kinetics and crystallite morphologies indicate that {110} facets are uncommon in CVD diamond, but existing models predict stable {110} growth. In addition, scanning probe analyses of CVD material often reveal atomically smooth {100} facets, whereas

conventional growth models predict atomic-scale roughening of the {100} face. In this study, we employ a multiscale approach to reconcile these discrepancies between model and experiment. The fundamental molecular diamond formation mechanisms are examined using quantum mechanical calculations of bonding and reaction kinetics. These calculations suggest a viable mechanism for the selective hydrogen-assisted removal of incorporated carbon from specific surface sites. The reaction kinetics for this etching process are estimated by the quantum mechanical calculations and are supplied as input to an atomic-scale kinetic Monte Carlo (kMC) deposition simulation. By comparing these kMC simulations to experimental measurements of growth kinetics and morphologies, we find that the addition of selective etching to the diamond growth mechanism serves to reconcile the model predictions with experimental observations.

11:30 AM I5.8
COMPREHENSIVE STUDY OF THE PHYSICAL MECHANISMS AFFECTING LINER CONFORMALITY OF PVD BARRIER AND SEED LAYERS. Peter L. O'Sullivan, F.H. Baumann, G.H. Gilmer, J. Dalla Torre, J.E. Bower, M. Cerullo and M.D. Morris, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

We study PVD (physical vapor deposition) of Ta and Ti diffusion barrier layers as well as Cu seed layers in the context of current and future interconnect generations. At present in industry, DC magnetron sputtering of neutral metal atoms is still adequate for providing acceptable liner integrity. However, we have derived a mathematical result which shows that the minimum step coverage (on the lower side-wall regions of trenches and vias) scales with the inverse square of the aspect ratio (AR) for trenches and with the inverse *cube* of AR for circular vias. Hence, for high AR features it is increasingly important to be able to model and simulate the PVD process with high accuracy. A valuable tool for rapidly predicting step coverage throughout entire features is 3D numerical topographic simulation. To this end, we have developed a general 3D level set code for the continuum model of profile evolution. Our computational tool has the flexibility to incorporate several important physical effects, such as non-uniform target erosion, non-cosine angular distributions, gas-phase scattering of sputtered atoms, re-sputtering, ionized species flux and statistical fluctuations in flux. Rather than embarking on case-by-case model-fitting (for empirical sticking factors) to experimental data (which may lack applicability to new geometries and/or feature sizes) it is crucial to develop predictive models based on rational model validation. In this regard we exploit auxiliary Monte Carlo simulations to provide accurate physical inputs (e.g. re-sputtering data as functions of energy and incident angle) for our continuum model of surface evolution. We compare our numerical results with experimental data for both centered and off-axis (on the wafer) trenches and vias to isolate the dominant physical effects for each of the materials that we study.

11:45 AM I5.9
THE INFLUENCE OF CLUSTERS ON VAPOR-DEPOSITED THIN FILMS: ATOMISTIC SIMULATIONS. Jacques Dalla Torre[1,2], George H. Gilmer[1], Frieder H. Baumann[1], Peter L. O'Sullivan[1]. [1]Bell Labs, Lucent Technologies, Murray Hill, NJ, [2]LAAS and LPST, CNRS, Toulouse, FRANCE.

Small clusters of atoms are present in the flux of material produced by sputtering and also by several other vapor deposition techniques. Furthermore, as a result of the large supersaturations present in most of these systems, a cluster of two or three atoms on a close-packed crystal surface is a super-critical nucleus. Therefore, the presence of such clusters in the sputtered flux can dramatically enhance the rate of two-dimensional nucleation of islands that is required for growth on these surfaces. In this talk we discuss the cluster distributions obtained using molecular dynamics simulations of the sputtering of Al and other materials. The effect of the clusters on facet reduction, film texture, surface roughness, and overall morphology is examined using the Monte Carlo simulator ADEPT. In addition to clusters generated by sputtering, we also simulate the effect of larger clusters obtained by vapor jets and other methods. Applications to the deposition of metal barrier-layer films and interconnect conductor metals are discussed.

SESSION I6: MODELS OF VAPOR DEPOSITION II
Chairs: Harry A. Atwater and Robert J. Kee
Wednesday Afternoon, April 26, 2000
Golden Gate A3 (Marriott)

1:30 PM *I6.1
CONTROL OF VAPOR DEPOSITION FOR ATOMIC-SCALE GROWTH OF THIN FILMS. R.L. Kosut, J.L. Ebert, S. Ghosal, S. Desa, SC Solutions, Santa Clara, CA.

In recent years, controlled atomic-scale growth of thin films has assumed an increasing role in the manufacture of high performance materials and devices. The exacting specifications of these thin films and heterostructures have stimulated both improvements in the deposition technologies, and in the incorporation of feedback and run-to-run control in the manufacturing process. This talk describes control strategies for improving performance of RF diode sputter deposition process for giant magnetoresistive (GMR) devices, and molecular beam epitaxy (MBE) of resonant tunneling devices (RTD). GMR multilayer devices consist of more than a dozen layers of ferromagnetic and non-magnetic conducting layers with film thickness in the general range of 20-40 Angstroms. Data obtained from Nonvolatile Electronics of Eden Prairie, MN showed unacceptably high variation in device properties from wafer-to-wafer. A detailed physical model of the sputter system showed that most of this variability was caused by fluctuations in the input RF power during plasma transients. A controller was designed and implemented at NVE which regulated the time-integrated target bias voltage. This control reduced wafer-to-wafer variability in GMR properties by more than half.
Similar to GMR devices, in epitaxial growth of InAs RTD's, it is important to deposit an exact number of monolayers. The oscillatory RHEED signal is used as the sensor to monitor the growth process. A model-based control scheme is described to regulate the effusion cell temperature, and to regulate the As cracker valve which controls the morphology of As deposited on an In-rich growth surface.

2:00 PM *I6.2
THREE NEW THEORIES MOTIVATED BY CONTROL PROBLEMS IN VAPOR DEPOSITION. David G. Meyer, John E. Hauser, Dept of Electrical and Computer Engineering, Boulder, CO.

Feedback control of vapor deposition processes presents unique challenges to the field of control theory. Many problems in control of vapor deposition are at or near the very limit of our understanding and capability in control. The authors have advanced three new control theories motivated by problems they have worked on in vapor deposition control. In this talk, these three theories are outlined and their application to vapor deposition control is explained.

3:00 PM I6.3
ATOMISTIC SIMULATION OF RF DIODE SPUTTER DEPOSITION OF GMR MULTILAYERS. W. Zou, X.W. Zhou, R.A. Johnson, H.N.G. Wadley, Department of Materials Science and Engineering, University of Virginia, Charlottesville, VA; D. Brownell, D. Wang, Nonvolatile Electronics, Inc.; S. Ghosal, D. Subhas, Robert Kosut, Jon Ebert, SC Solutions, Santa Clara, CA.

Radio frequency (RF) diode sputtering has been used for the growth of giant magnetoresistive (GMR) metal multilayers. Control of the atomic-scale structure of the surfaces and interfaces within these films is critical for GMR applications. A systematic series of experiments have been conducted to evaluate the dependence of magnetic properties and magnetoresistance upon growth conditions (i.e. background pressure, input power) for NiFeCo/CoFe/CuAgAu multilayers with different CuAgAu thickness during RF diode sputter deposition using an argon plasma. Atomic force microscopy results have shown that the background pressure and plasma power have large effects upon column width and surface morphology that eventually affect GMR properties. By using a newly developed embedded atom method (EAM) alloy potential, a multiscale modeling study has been used to investigate the layer by layer growth phenomena and to identify the origin of the relationships between the experimental observations and growth conditions.

3:15 PM I6.4
SIMULATION OF 3D FILMS DEPOSITED BY GLANCING ANGLE DEPOSITION USING *3D-FILMS*. T. Smy, Dept. of Elec., Carleton University, Ottawa, ON, CANADA; D. Vick, M.J. Brett, S.K. Dew, A.T. Wu, J. Sit, K. Harris, Dept. of Electrical Eng., University of Alberta, Edmonton, AB, CANADA.

A novel three dimensional ballistic deposition simulator *3D-FILMS* has been developed for the modeling of thin film deposition and structure. The simulator features a ballistic transport algorithm to model incident species with angular distribution appropriate to physical vapour deposition systems. Two-tiered data structuring is employed in order to enable the simulator to run using memory resources available to workstations. Deposition is modeled as a ballistic Monte Carlo process which incorporates nucleation, self-shadowing, adatom mobility and a variety of physical effects, which include non-unity sticking, resputtering and local annealing phenomena. *3D-FILMS* provides a complete 3D depiction of the film and its microstructure and can also produce information on local film density and differential and total surface area. The simulator has been applied to a unique class of thin films grown by the technique of GLancing Angle Deposition (GLAD). Simulation can provide a powerful tool toward understanding and ultimately exploiting the

morphology of this class of thin films. These films exhibit low bulk density due to an internal structure consisting of isolated microcolumns, which can be engineered into a variety of 3D forms. Because of their inherent 3D morphology, created by a combination of complex substrate motion and 3D shadowing, GLAD films represent an ideal test subject for 3D simulation. SEM images of films are presented together with simulation results, which correctly reproduce aspects of column morphology, column growth competition and extinction, and film bulk density. The simulator can correctly reproduce aspects of column morphology, column growth competition and extinction, and film bulk density. *3D-FILMS* is expected to prove a powerful tool for modeling the properties of real films such as porosity and material dependence effects and to investigate and optimize the effects of process parameters on GLAD structure.

3:30 PM I6.5
THE ROLE OF REACTOR-SCALE SIMULATION IN MULTISCALE MODELING OF CVD DIAMOND DEPOSITION.
D.S. Dandy, Colorado State University, Dept. of Chemical Engineering, Fort Collins, CO; C.C. Battaile, Sandia National Laboratories, Albuquerque, NM; D.J. Srolovitz, Princeton University, Princeton Materials Institute, Princeton, NJ; J.E. Butler, Naval Research Laboratory, Washington, DC; I.I. Oleinik and D.G. Pettifor, Oxford University, Dept. of Materials, Oxford, UNITED KINGDOM; S.J. Harris, Ford Scientific Research Labs, Chemistry Department, Dearborn, MI.

One dimensional reactor models have proven to be successful when predicting gross qualitative features such as steady state deposition rate and the gas-phase temperature profile in geometrically simple diamond deposition systems. However, to refine the kinetic descriptions of elementary growth processes and develop predictive models of morphology evolution, it is necessary to utilize more accurate, spatially-resolved reactor simulations. To this end, we have applied the governing conservation equations for momentum, mass, and energy in axisymmetric coordinates to the growth of diamond in a moderate-pressure (100 Torr) microwave reactor. The model includes full multicomponent transport with homogeneous kinetics in the gas phase, and heterogeneous chemistry derived from kinetic Monte Carlo calculations and first-principles quantum mechanical evaluation of bonding and kinetics. Although the gas phase processes occur, for all practical purposes, at local thermodynamic equilibrium, a plasma fluid model is applied to predict electron density, electron temperature, and local energy density, and this information is incorporated into the gas-phase energy equation. Optimal values for inlet concentrations and microwave power are identified for maximization of deposition rate and film radial uniformity. The spatially-dependent surface concentrations of important gas species predicted by the reactor model are used in mesoscale kinetic Monte Carlo calculations to examine deposition pathways and to simulate crystal growth; and these concentrations are also used in polycrystalline morphology evolution models to examine uniformity and texture of films as they grow.

3:45 PM I6.6
MODELING OF IONIZED MAGNETRON SPUTTERING OF COPPER.
Max O. Bloomfield, David F. Richards, Timothy S. Cale, Rensselaer Polytechnic Institute, Troy, NY.

Computer simulations are used to study ionized physical vapor deposition, with ionized magnetron sputtering of copper as the primary system of interest. The effects of sputtering-ion energy and sputtering-ion angular flux distributions on the evolution of sub-micron scale features during IPVD are explored using the EVOLVE simulator. Our goal is to develop semi-quantitative engineering relationships that accurately predict the trends in experimental responses to changes in operating conditions. A sticking-factor model is used to describe deposition by neutrals. The sticking-factor of incident Cu atoms can depend on arrival angle and energy. Copper ions can also become part of the growing film. Energy and angular dependent sputter yields for both copper and argon ions are taken from MD simulation results. Sputtered material is ejected from the surface, tracked through the gas phase, and allowed to redeposit. Redeposition is also modeled via a sticking-factor based approach. The redistribution of film material results in non-intuitive profiles and complex relationships between final profiles and process parameters such as sample bias and neutral-to-ion flux ratios.

4:00 PM I6.7
COMPREHENSIVE REACTOR SCALE MODELING OF III-V TERNARY COMPOUND GROWTH BY MOVPE.
Roman A. Talalaev, Eugene V. Yakovlev, Sergey Yu. Karpov, Soft-Impact Ltd, St. Petersburg, RUSSIA; Yuri A. Shpolyanskiy, Inst. for Fine Mechanics and Optics, Computer Technology Dept, St. Petersburg, RUSSIA; Yuri N. Makarov, Univ. Erlangen-Nürnberg, Fluid Mechanics Dept, Erlangen, GERMANY; Samuel A. Lowry, CFD Research Corporation, Huntsville, AL.

Development of surface chemistry models still remains one of the critical issues in III-V MOVPE modeling. We propose a novel quasi-equilibrium approach to simulate surface chemistry. The basic advantage of the approach originates from combination of kinetic and thermodynamic description of the surface processes. This allows to reduce significantly the number of model parameters and to avoid a fitting procedure which is usually used to estimate the unknown rate constants. The quasi-equilibrium approach is applied to study of surface processes during MOVPE of GaAs, InGaAs, AlGaAs, and InGaP. A novel mechanism limiting growth rate at low temperatures is proposed - desorption of hydrocarbon species from the growth surface. The application of the model to MOVPE of GaAs shows the quantitative agreement between the computed and measured growth rates in the wide range of operating conditions without any fitting procedure. Verification of III-V ternary alloy MOVPE models is performed by 3D simulation of AlGaAs, InGaAs and InGaP growth in a commercial horizontal AIX-200 epitaxial reactor. In order to predict accurately the temperature and species distribution affecting the growth rate and layer composition, the gas flow, heat transfer and mass transport phenomena have been investigated. Radiation heat exchange, conjugate heat transfer and heat conduction in solid blocks of the reactor (susceptor, reactor walls) are taken into account. Growth rate, composition and uniformity of the epitaxial layers are found to be in good agreement with the experimental data.

4:15 PM I6.8
A MODULAR FRAMEWORK FOR INTEGRATED, MULTISCALE SIMULATION OF CHEMICAL VAPOR DEPOSITION.
David G. Goodwin, Eduardo A. Repetto, Brian Platt, Martha A. Gallivan, Michel Jabbour, Kaushik Bhattacharya, Michael Ortiz, Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA; Laxminarayan L. Raja, Robert J. Kee, Engineering Division, Colorado School of Mines, Golden, CO.

Simulation of thin film growth by chemical vapor deposition requires modeling physical processes occurring over a wide range of length and time scales, from atomic-scale crystal nucleation and growth, through microstructure evolution on mesoscopic scales, to macroscopic reactor-scale gas-phase species and energy transport. These processes are often coupled, and must therefore be simulated together. However, the computational expense of a fully-coupled high-resolution simulation is prohibitive, requiring one to use high-resolution (for example, atomic scale) models only where required, and lower-resolution (continuum) models elsewhere. Here we describe a flexible, modular, object-oriented software environment for multiscale, multi-resolution CVD simulation. Physical models are selected from a library of models of varying degrees of fidelity/expense, and may be quickly assembled to form a complete, dynamic "virtual reactor" simulation. Models of film microstructure evolution provided include Kinetic Monte Carlo and continuum PDE models, along with simpler rate-equation models Use of this environment to simulate MOCVD of YBCO will also be described.

4:30 PM I6.9
OPTIMAL DESIGN OF REACTORS FOR METALORGANIC VAPOR PHASE EPITAXY OF GROUP III NITRIDES.
R.P. Pawlowski, C. Theodoropoulos, T.J. Mountziaris, SUNY at Buffalo, Dept. of Chemical Engineering, Buffalo, NY; H.K. Moffat, J. Han, Sandia National Laboratories, Albuquerque, NM.

Metalorganic Vapor Phase Epitaxy (MOVPE) has emerged as the technique of choice for growing thin films and structures of group III-nitrides from vapors of metal alkyls and ammonia. The objective of this work is to address the optimal design of vertical rotating disk and stagnation flow MOVPE reactors in order to achieve film thickness uniformity over large area substrates. A serious problem in the design of such reactors is the control of pre-reactions between metal alkyls and ammonia that form stable adducts. These adducts can form oligomers, higher order n-mers and eventually aerosol particles that ruin film quality. Furthermore, the adducts can condense on cool reactor surfaces, upstream of the substrate, thus depleting the rate limiting group III precursor. Gas inlets that preserve the axial symmetry and enable alternating feeding of the precursors through coaxial rings were designed. The growth of GaN films from trimethyl-gallium and ammonia was used as a typical example. A fundamental reaction-transport model of the MOVPE process including gas-phase reactions and gas-surface interactions has been developed. The coupled partial differential equations were solved using a state of the art finite element code (MPSalsa) developed at Sandia National Laboratories that employs the CHEMKIN libraries to provide a rigorous treatment of multi-component ideal gas phase kinetics, surface kinetics and transport. The model was validated by comparing its predictions with growth rate data obtained from a vertical rotating disk reactor. The relative role of various reaction and transport pathways leading to film growth was investigated by sensitivity analysis. Performance diagrams for industrial-size

stagnation flow and rotating disk reactors were developed by varying the reactor geometry and operating conditions. Optimal conditions were identified leading to uniform films over large area substrates.

4:45 PM I6.10
VISUALIZATION OF POLYCRYSTALLINE THIN FILM GROWTH FOR PVD. Jie Zhang, James B. Adams, Arizona State Univ, Dept of Chemical Bio and Materials Engineering, Tempe, AZ.

We present a model for two-dimensional simulation of polycrystalline thin film growth during physical vapor deposition (PVD). The model is based on the concept of describing the crystal surface in terms of preferred facets. The initial location, size, shape and orientation of the nuclei are randomly determined, and crystallographically appropriate facets are created. The rates of diffusion between facets are determined from previous Kinetic Lattice Monte Carlo (KLMC) simulations. Dynamic facet arrays, fixed grain boundary arrays and node arrays are created to control the growth and interaction of multiple grains. A segmental method is used to describe facets and grain boundaries. The model is first applied to the study of deposition of Cu on both flat surfaces and in trenches. The software is Windows based and has an integrated Graphic User Interface, within which a user can input experimental and simulation data, visualize the nucleation and growth of the grains, and obtain the final grain structure and texture.

SESSION I7: POSTER SESSION: NEW METHODS, MECHANISMS AND MODELS OF VAPOR DEPOSITION

Wednesday Evening, April 26, 2000
8:00 PM
Salon 1-7 (Marriott)

I7.1
COMPUTATIONAL EXPERIMENT ON CVD OF SiC: GROWTH RATE, C/Si-RATIO, PARASITIC PHASE FORMATION. A.N. Vorobev, A.E. Komissarov, M.V. Bogdanov, Inst for Fine Mechanics and Optics, Computer Technology Dept, St. Petersburg, RUSSIA; A.A. Lovtsus, O.V. Bord, S.Yu. Karpov, Soft-Impact Ltd, St. Petersburg, RUSSIA; Yu N. Makarov, Univ of Erlangen-Nurnberg, Fluid Mechanics Dept, Erlangen, GERMANY.

Computational experiment on chemical vapor deposition (CVD) of SiC epilayers in a vertical rotating disc reactor is carried out basing on original model recently developed. The model accounts for the heat and mass transfer in the reactor coupled with spontaneous condensation of silicon vapor in the gas phase. Nucleation of Si clusters is considered using the Becker-Dring approach. Transport of the clusters and their growth/evaporation are treated using the first three moments of size partition function of the clusters. Thermoforetic force is found to be important for prediction of cluster distribution over the reactor. Growth rate, carbon-to-silicon ratio, formation of parasitic (graphite or silicon) phases on the surface during growth as a function of operating parameters (silane and propane inlet flow rates, pressure, temperature) varied in a wide range are computed. Regression analysis is used to predict optimal growth conditions under which the nucleation and the parasitic phase formation can be avoided. Particular attention is paid to three-dimensional gas-dynamic effects and effects on cluster nucleation on growth of epitaxial SiC films. The theoretical results are in good agreement with experimental observations available.

I7.2
BONDING AND COHESIVE PROPERTIES OF THE COBALT/ALUMINA SPIN VALVES. I.I. Oleinik, E. Yu. Tsymbal and D.G. Pettifor, Oxford University, Department of Materials, Oxford, UNITED KINGDOM.

Spin-dependent tunneling (SDT) magnetic junctions are promising candidates for use in magnetic RAM (MRAM) chips, and field detection applications (read heads and sensors). SDT spin valves are grown by depositing several monolayers of aluminium film on top of a ferromagnetic layer, followed by thermal- or plasma-assisted oxidation to create a pinhole-free alumina tunneling barrier. Previous studies have revealed the critical influence of the chemistry and structure of the ferromagnet metal/alumina interface on both sign and magnitude of the tunneling current in SDT junctions. We have performed a detailed first-principles study of the structure and bonding at the cobalt/alumina interface in order to understand the relationship between magnetic properties, local bonding environment and cohesion at the interface. Both Al- and O- terminated interfaces were considered and full geometry optimization of the structure was done by self-consistent spin-polarized calculations within density functional theory and the generalized gradient approximation. The nature of the cohesion at the interface was thoroughly examined. We have found that magnetic effects make an appreciable contribution to the cohesion in case of aluminium terminated interface. We will discuss the character of the metal-oxide bonding based on the predicted charges and bond orders.

I7.3
A CONTINUUM MODEL OF KINETIC ROUGHENING AND COARSENING IN THIN FILMS. K. Bhattacharya, M. Ortiz, E.A. Repetto, Y.C. Shu, California Institute of Technology, Pasadena, CA.

We present a phenomenological continuum model of film growth based on a series expansion of the deposition flux in powers of the profile gradient, consideration of the energetics of the film/substrate interface, stress and plasticity effects and the enforcement of Onsager's reciprocity relations. The interfacial term, which operates at very small thicknesses, is nonconservative and breaks the $\pm h$ symmetry of the remaining terms in the kinetic equation. By virtue of this term, very thin flat films are predicted to be stable within an appropriate range of parameters, and to loose stability and become rough at a well-defined critical thickness. This instability effectively provides a island nucleation mechanism. For thick films, the rate processes envisioned in the model favor a characteristic slope for the film profile, a feature which is in keeping with observation for a number of systems including YBCO films. The enforcement of reciprocity ensures the existence of a kinetic potential and enables the use of direct methods of the calculus of variations. Within this framework, we provide an explicit construction for the coarsening of the film profile based on a sharp interface approximation. The construction predicts characteristic exponents for the evolution of grain size and film roughness which are in close agreement with the observational evidence for YBCO. The predictions of the construction are also born out by numerical tests. We also present numerical simulations showing the influence of the different terms in our model on the film evolution.

I7.4
EXCIMER PULSED LASER ABLATED MOLECULAR BEAM EVAPORATION FOR THE DEPOSITION OF BINARY SKUTERUDITES. H.-A. Durand, K. Nishimoto, K. Ito, I. Kataoka, JAE Ltd., Tokyo, JAPAN.

The family of materials having the skutterudite crystallographic structure have recently attracted interest because of their extra-ordinary electrical and thermal transport properties, as well as their peculiar magnetic qualities. Particularly, the group of cobalt antimonide skutterudites has been referred to as electron crystals and phonon glasses. With the goal to prepare skutterudite thin films, laser ablation is unique in its capacity to transfer skutterudite target's complex composition untouched to substrates while providing an hyperthermal beam that has a positive influence on thin film growth. We use a pulsed excimer laser at 193 nm to evaporate skutterudites targets in ultra-high vacuum and deposit thins films on silicon wafers and fused silica substrate. We have studied the composition and crystallographic structure of the deposits as a function of substrate temperature and target to substrate distance. Deposits are skutterudite poli-crystals of several hundreds nanometers. We investigated the electrical as well as the thermal transport properties of thin films having the desired phase. These compare well with value reported for the bulk mono-crystals. The scattering that may happen at the boundaries of grains appears to be balanced by the intrinsic high quality of the mono-crystalline grains. Such a result opens the way to electric thermo-generation applications using thin films.

I7.5
AFTER-NUCLEATION SURFACE PHENOMENA, SURFACE SMOOTHING AND MORPHOLOGICAL DESTABILIZATION IN CHEMICAL VAPOR DEPOSITION. Oleg A. Louchev, Yoichiro Sato, Hisao Kanda, National Institute for Research in Inorganic Materials, Tsukuba, JAPAN.

Vapor growth of films exhibits a variety of different surface morphologies which are very sensitive to the variations of operating parameters. In great part the resulting morphology of films is predetermined by after-nucleation morphology of surface and phenomena taking place during the transition period to the continuos growth. In this communication we consider the case when typical dimensions of after-nucleation profiles are much lower than the mean free path of gas species and the effect of ballistic self-shadowing of the surface may induce instability. We represent a model based upon a set of continuum integral-differential equations for surface transport-kinetical phenomena including adsorption, thermal desorption, secondary adsorption occuring after desorption, precursor decomposition, surface diffusion and kinetics of atoms incorporation into the solid phase. We show that morphological destabilization induced by ballistic self-shadowing takes place in situations with two conditions: (i) the surface concentration of precursor is held far from adsorption/

desorption equilibrium and (ii) the length scale of after-nucleation profile is much larger than surface diffusion lengths of precursor and deposit. In this case the induced instability may lead to the formation of columnar structures. In case when the adsorption/desorption equilibrium of precursor is achieved or length scale of after-nucleation profile is lower than surface diffusion lengths the surface concentration of deposit and the growth rate are equalized over the surface and the amplitude of the surface profiles are not amplified, and the initial profiles scales tend to remain during the growth stage. The model shows the possibility for smoothing of the after-nucleation profiles caused by an increase of adsorption energy in the surface cavities for the case when separation length between the nuclei tends to the level of 0.1 micron. The experimentally feasible steps for improving morphology of films and possibility of onset of oscilatory growth modes caused by non-linear incorporation kinetics are discussed.

I7.6
QUANTITATIVE COMPARISON OF RHEED KINEMATIC SIMULATIONS, RHEED DYNAMICAL SIMULATIONS, AND RHEED EXPERIMENTS FOR BIAXIALLY-TEXTURED POLYCRYSTALLINE MgO FILMS. R.T. Brewer[a], Y. Chen[b], J.R. Groves[c], P. Arendt[c] and H.A. Atwater[a]. [a]Thomas J. Watson Laboratories of Applied Physics, California Institute of Technology, Padadena, CA, [b]Courant Institute of Mathematical Sciences New York University, New York, NY, [c]Los Alamos National Laboratories, Los Alamos, NM.

To date, reflection high energy electron diffraction (RHEED) has been used to characterize properties of single crystal surfaces during thin film growth, but has not been applied to understanding the microstructural evolution in real time in polycrystalline thin film growth. We present here a comparison of RHEED experiments for biaxially-textured MgO thin films with the results of a kinematic RHEED model and also with dynamical simulations of RHEED intensities. We have developed a computer simulation that calculates RHEED patterns based on a dynamical scattering, multi-slice model. The dynamical simulation technique is absolutely stable and requires computation time proportional to only M*N*log(M*N), where M is the number of beams and N the number of slices, representing a significant computational advance in RHEED calculations. Mosaic polycrystalline MgO RHEED patterns approximated using the dynamical scattering based simulation have been compared to results from our simulation based on analytic calculation of RHEED patterns in the kinematic approximation. The two simulation results are compared for given values of electron beam incidence angle, polycrystalline texture, in-plane orientation distribution, and grain size. Using the simulation results, we can quantitatively determine how RHEED spot shapes and relative intensities depend on the mosaic film characteristics. RHEED patterns taken at 25 keV with incidence angle in the range 1-5 degrees from 10 nm thick nominally [100]-textured MgO films grown on amorphous Si_3N_4 films by IBAD were analyzed by comparing experimental RHEED spot shapes and relative intensities with those predicted by the simulation results. For some films, an additional 200 nm thermally-grown MgO homoepitaxial layer was grown on top of the IBAD MgO layer. Results are also compared to X-rayrocking curve film analysis, and the quantitative correlation between biaxial texture and model-based RHEED analysis will be discussed.

I7.7
ATOMISTIC MODELING OF ULTRATHIN Fe FILMS ON Cu(111). A. Rakotomahevitra and L.T. Wille, Department of Physics, Florida Atlantic University, Boca Raton, FL.

Theobald *et al* (Phys. Rev. **59**, (1999) 2313) have shown, using photoelectron diffraction in the scanned-energy mode, that at 300K iron grows pseudomorphically on Cu(111) up to a thickness of about two equivalent monolayers. Another finding was that above this thickness the film becomes bcc with (110) orientation. Ohresser *et al* (Phys. Rev. **59**, (1999) 3696) have compared the pulsed-laser deposition (PLD) films to the thermal deposition prepared Fe/Cu(111) films and connected the system's morphology to its magnetic properties. We used the embedded-atom method (EAM) to perform molecular-dynamics (MD) simulations of up to four iron films on Cu(111). We simulate the deposition, by integrating the equations of motion under constant-pressure-constant-enthalpy periodic boundary conditions, with Parinello-Rahman molecular dynamics formulation. This technique is well suited to the study of a possible phase transformation in solids. A comparison between random and ballistic deposition of iron adatoms was performed. The main observations are i) an interdiffusion between Fe and Cu; ii) a phase transformation from fcc to bcc as a function of film thickness, both in good agreement with experiment.

I7.8
MOLECULAR DYNAMICS SIMULATIONS OF FILM GROWTH ON HEXAGONAL AB AND ABC PACKED SUBSTRATES USING LENNARD-JONES POTENTIALS. A.G. Jackson, M. Benedict, M. Jackson, AvXm Partnership, Dayton, OH; J. Maguire, AFRL/MLMR, WPAFB, OH.

Growth of thin films is of considerable interest to industry and government. Simulating the growth of films of high complexity is difficult and time consuming, and hence new methods for these simulations are being sought in this Laboratory. Molecular dynamics offers excellent capabilities for simulating growth of real materials as thin films, but the time to compute the simulations is high. In this report, Lennard-Jonesium substrates in hexagonal geometry are used for constructing a thin film using small clusters of atoms arriving at the substrate with thermal energies. The procedure is to collide the cluster with the substrate, equilibrate, and then use the cluster-substrate surface as the surface for a new cluster collision. This is repeated until a film is generated on the substrate. Visualizations of the film during stages of formation allow rough estimation of surface diffusion effects, useful for rough estimates of surface diffusion coefficients. Visualizations of simulations will be presented which allow observations of the deposited atoms as a function of time, as well as observation of equilibration of the clusters onto and into the surface.

I7.9
NITROGEN INCORPORATION AND GROWTH KINETICS OF GaAsN/GaAs EPILAYERS GROWN BY MOVPE. Laurent Auvray, Hervé Dumont, Jacues Dazord, Yves Monteil, Jean Bouix, Villeurbanne Cedex, FRANCE.

The Ga(In)AsN/GaAs system is an attractive alternative to the conventional InGaAsP/InP system for the fabrication of emission devices for fiber-optical telecommunications at 1.3 μm. It remains that incorporation of nitrogen greatly depends on the growth parameters, In content, but is larger than thermodynamical prevision. In this context, we present a study on the growth mechanism of $GaAs_{1-x}N_x$ epilayers (x<4%) obtained by Metal Organic Vapor Phase Epitaxy. The alloy was grown on GaAs (001) substrates (2° misoriented) using N_2 as the carrier gas and the combination of precursors: trimethylgallium, arsine(AsH_3) and dimethylhydrazine (DMHy). Epilayers were 0.2-0.3 μm thick and characterized by X-ray diffraction and photoluminescence. Some of the layers were capped with GaAs (50nm) for subsequent thermal treatment to improve optical properties.
The N incorporation behavior was investigated in the growth temperature range 500-600°C and the surface morphology was observed by AFM. It was observed that the temperature-dependence of the nitrogen incorporation exhibits two regimes. The N composition varies slowly with 500°C <T < 560°C with an activation energy of 0.6eV. At 530°C, the nitrogen content x was an highly nonlinear function of the gas-phase composition indicating a surface-controlled reaction mechanism with competitive adsorption of arsine and DMHy. For T> 560°C, N decreases exponentially with E_a=3.7 eV interpreted in terms of nitrogen desorption. However, good surface morphologies show a bunched step/terrace structure for N contents up to about 2%. Above this limit, terraces were less and less visible with appearance of cross-hatch lines relieving stress due to lattice- mismatch. A kinetic model of surface reaction will be proposed to take account for experimental results and those of literature.

I7.10
DIAMOND SYNTHESIS ON GLASSY SUBSTRATES WITH COMPLETELY CLOSED REACTION CHAMBER. Rie Hayashi, Fumitomo Onishi, Mayu Uede, Yoshiki Takagi, Teikyo Univ of Science & Technology, Yamanashi, JAPAN.

Recently, many results were reported by many universities and companies all over the world for diamond particles or thin films synthesized on crystalline substances, such as molybdenum, silicon etc. But diamond on noncrystalline substances, or on amorphous were rarely reported. We hereby report diamond synthesized on quartz glass substrate with completely closed gas phase reactor. The reactor we used was very unique for diamond synthesis, no reaction gas was introduced to the chamber and no reactant gas was evacuated from it. Graphite rod was used as carbon source, mounted the center of the chamber, about 3-4mm under the rod, the quartz glass substrate was set. Hydrogen gas was introduced into the reaction chamber with the suitable initial pressure, and then sealed. Graphite rod was heated and controlled with Joule heating. Substrate temperature was about 750 degree Celsius. With SEM photographs, crystal shaped particles were observed. And with Raman spectrometry, Raman peaks were assigned as typical diamond peaks. With these results, we clearly confirmed that the deposits on quartz glass substrates were diamond particles, the first time in the world.

I7.11
NOVEL EMISSIVITY COMPENSATED PYROMETER FOR PROCESS TEMPERATURE MEASUREMENTS IN ROTATING DISK MOCVD REACTOR. Vadim Boguslavskiy, Alex Gurary, Jeff

Ramer, Matt Schurman, Ameesh Patel, Rick Stall, Emcore Corp., Somerset, NJ.

Accurate and repeatable wafer temperature measurement during epitaxial deposition is one of the major and largely unresolved problems of modern semiconductor manufacturing processes. Different types of non-contact pyrometers are presently used with different degree of success. A typical problem for all pyrometer techniques is unknown or varying target emissivity. It is especially challenging in the case of epitaxial deposition of the compound semiconductor structures, when the spectral directional emissivity of the wafer can vary from less than 1% to more than 99%. Commonly used multi-wafer reactor configuration requires segregation of measurements performed on the wafer and wafer carrier surfaces. In this work, we report on a novel emissivity compensated pyrometer that allows accurate and repeatable wafer temperature measurement in production scale high speed rotating disc MOCVD reactor. This pyrometer has been developed to be implemented into large-scale production environment and has a simple in-situ calibration procedure. A special statistical algorithm that separates temperature measurements, performed on the wafers and on the rotating carrier, is described. We present a comprehensive analysis and experimental results on the subject of temperature measurement accuracy and repeatability in emissivity compensated pyrometry that establishes the limits of this technique. We have demonstrated temperature repeatability of ± 1 deg C with this instrument. Application of this technique to the growth of highly temperature sensitive InGaAsP/InP structures demonstrates its accuracy and repeatability, and the dramatic improvement it brings to the epitaxial process development and maintenance.

I7.12
HIGH-J_c YBCO CONDUCTORS FABRICATED BY MAGNETRON DEPOSITION. S. Gnanarajan, A. Thorley, A. Katsaros, J. Herrmann, A. Molodyk and N. Savvides, CSIRO Telecommunications and Industrial Physics, Sydney, AUSTRALIA.

We have fabricated high-J_c YBCO coated conductors using IBAD and magnetron sputtering techniques. Polished Hastelloy tapes were coated with a biaxially aligned YSZ buffer layer ($\sim$300 nm) by combining IBAD and magnetron deposition. X-ray pole-figures and ϕ-scans show the buffer layers to have a (111) pole in the ion beam direction (55° to the substrate normal) and FWHM $\Delta\phi = 13°$. Epitaxial YBCO thin films were deposited onto the YSZ/Hastelloy substrate by unbalanced magnetron sputtering using a stoichiometric YBCO target. The YBCO films have (103) $\Delta\phi = 10°$ and $J_c(77\ \mathrm{K}) = 1.2 \times 10^6\ \mathrm{Acm}^{-2}$.

I7.13
STRONGLY (111) ORIENTED METALLIZATION BY ION PLATING METHOD. Toshio Kudo, Susumu Sakuragi, Hiroyuki Makino, Shin Masui, Kimio Kinoshita, Masaru Tanaka, Sumitomo Heavy Industries, Ltd., Research and Development Center, Hiratsuka, JAPAN.

Our ion plating (URT-IP) method has the advantage of self-surface-cleaning effect. By means of the URT-IP, Cu films were directly deposited on blanket wafers without surface cleaning. Each wafer is covered with an underlayer, a Cu seed layer or a TaN barrier. The Cu seed layer itself has the (111) texture and the TaN barrier an amorphous-like texture. The surface roughness of Cu seed layer is about four times bigger than that of TaN barrier. Strong Cu(111) texture is observed for both of Cu seed layer and TaN barrier. The (111) orientation of Cu films, however, is dependent on the surface condition of underlayers: the crystal orientation is in preference to the surface roughness. The strong Cu(111) orientation from the first deposition stage comes from self-surface-cleaning effect: positive ions accelerated by weak self-bias-voltage assist Cu deposition coming simultaneously into the wafer surface. In the same way, Cu films were deposited on trench pattern wafers without surface cleaning. There is a striking contrast between the underlying Cu seed and TaN barrier layers. The Cu film on the TaN barrier has a much stronger (111) texture than that on the Cu seed layer. Cu wires in trenches maintain the strong (111) orientation for the TaN barrier, while still have the weak orientation for the Cu seed. The URT-IP method has another advantage: strongly oriented Cu(111) texture can be formed in trenches. It is essential that the underlayer is amorphous like the TaN barrier. In this paper we will also report the result of strongly (111) oriented Pt thin-film.

I7.14
ATOMIC LAYER CHEMICAL VAPOR DEPOSITION OF TiN ON Si(100) AND Si(111). Hyeongtag Jeon, Jae-Hyoung Koo, Young-Seok Kim, Young Do Kim and Kyoung-Soo Yi*, Division of Materials Science and Engineering, CPRC, Hanyang Univ., Seoul, KOREA. *Genitech Co. Ltd., Taejon, KOREA.

A TiN film has been applied as a diffusion barrier for Al metallization in ULSI device because it shows a very low resistivity, high melting point, thermal stability and good adhesion characteristics. This TiN film can be deposited by various methods such as reactive sputtering, low pressure CVD and metal-organic CVD. Although the TiN thin film deposited by PVD such as sputtering method exhibits better thin film quality than that of CVD method due to the high film density and low impurity content, the need for CVD processing technique for TiN film is increasing with scaling down of ULSI device because of a poor step coverage of the sputter-deposited TiN film for high aspect ratios of contact and via holes. However, CVD method also exhibits the problems such as the high process temperature, particles generation and high impurity contamination. For these reasons, the new methods of thin film growth have been suggested and we developed the new deposition method which is the Atomic Layer Chemical Vapor Deposition (ALD) technique to improve the combined problems of PVD and CVD methods. The advantages of this ALD method over other deposition methods are the low process temperatures, low impurities content, conformal step coverage and excellent thickness uniformity over large substrate areas. In this study, we deposited TiN film successfully at 450°C and below by ALD method on p-type Si (100) and (111) substrates. In this ALD system, the $TiCl_4$ and NH_3 gases were supplied, separately and Ar purge gas was added between the source and reactant gases to suppress the direct reaction. The process parameters of total pressure and deposition temperature were kept at a constant values of 2 Torr and 450°C and were varied to examine the TiN thin film characteristics. The main purpose of this study is to investigate the effect of TiN film on the different orientation of Si substrates. The TiN films have been grown on these Si substrates, and the physical and electrical characteristics were investigated by using AES, XRD, TEM, AFM, RBS and four point probe. For this process, the deposition rate of TiN thin film was nearly a quarter-monolayer per one cycle. The composition of TiN films grown by ALD method was almost 1:1 of Ti:N, and exhibited very low chlorine content below the detection limit of AES. The resistivities of TiN films deposited on Si substrates were about 100-150 $\mu\Omega$·cm that were very low compared to TiN film grown by other CVD methods. The XRD results exhibited the formation of crystalline TiN with the strong peak of (200) and the TEM results showed the randomly oriented columnar structure. The densities of TiN films measured by RBS were about 4.85-5.1 g/cm^3. Also, the surface roughness of TiN film were measured by AFM. With these results, we can summarize that the TiN films deposited on Si (100) and (111) substrates by ALD method exhibited excellent physical and electrical properties compared to other deposition methods.

I7.15
PULSED LASER DEPOSITION OF HIGH QUALITY NITRIDE THIN FILM WITH ASSISTANCE OF LASER INDUCED NITROGEN PLASMA. X. Chen, Gan Wu, Yonghua Li, J. Yang, Z. Lei, Lanzhou Institute of Physics, Lanzhou, CHINA; Meicheng Li, Harbin Institute of Technology, Harbin, CHINA.

High quality nitride thin films (like GaN, BN, AlN, TiN)are very much in demand for advanced electronic devices and have attracted mucn attention. In this paper, we report our experiment results of Pulsed Laser deposition of GaN, BN an TiN thin films with the assistanc of laser induced Nritrogen plasma. A specially desighed device was used to inject micro-drops of liquid Nitrogen into the intense laser beam. It has been found that the stoichiometry and crystalization of the film deposited under this condition were significantly imporved due to the existance of the highly activated Nitrogrn plasma.

I7.16
MICROSTRUCTURE AND NANOMECHANICAL PROPERTIES OF DIAMONDLIKE CARBON THIN FILMS PREPARED BY PULSED LASER DEPOSITION IN VARIOUS ATMOSPHERES. Q. Wei, S. Yamolenko, J. Sankar, Dept of Mechanical Engineering, North Carolina A&T State University, Greensboro, NC; A.K. Sharma, Y. Yamagata and J. Narayan, Dept of Materials Science and Engineering, North Carolina State University, Raleigh, NC.

We have investigated the effect of chamber pressure and atmosphere on the nanomechanical properties of diamondlike carbon thin films prepared by pulsed laser deposition. The DLC films were deposited in various atmospheres such as nitrogen and argon at different pressures. We used Raman spectroscopy and transmission electron microscopy (EELS and radial distribution function analysis) to study the bonding characteristics of the DLC films. Nanoindentation measurements were carried out on various samples prepared under different conditions to study the effect of chamber pressure and atmosphere on the Youngs modulus and nano-hardness of the films. It was found that reduced vacuum leads to softer DLC films. This can be understood in terms of thermalization of the laser plasma due to increased possibility of collision.

I7.17
HYDROGEN PROMOTED COPPER ATOMS MIGRATION IN THE HIGH PRESSURE ANNEAL PROCESS(HIPA). Takao Fujikawa, Machinery Company, Kobe Steel Ltd, Takasago, JAPAN; Takashi Ohnishi, Toshiki Sato, Technology Development Group, Kobe Steel Ltd, Kobe, JAPAN.

To meet the requirement of lower processing temperature in the HiPA, hydrogen added PVD of Cu was investigated. Experimental results revealed that hydrogen addition is effective to lower the processing temperature by softening the PVD-Cu film and romoting the grain growth.

I7.18
SCIENTIFIC BASIS FOR DEVELOPING ADVANCED MATERIALS BY CVD-METHOD. Valery A. Voronin, Vladymir N. Sivers, Last Co, Lviv, UKRAINE.

The main objective of the paper is the development of a general theory and its implementation for the epitaxial growth of semiconductor materials by CVD-method. On the basis of the system study of the chemical nature of processes it is necessary to build a graph-model which would reflect all possible chemical and phase changes, as well as atomic and molecular forms. The graph-model is a structural topological matrix, STM, with atoms and molecular forms at the tops and chemical and phase changes presented at the connecting ribs. Thereby, the chemical processes and all the available atomic and molecular forms of the system components can be established. The methodology developed allows to create a mathematical model of the equilibrium process, if the STM is viewed as a stationary equilibrium system. Self-agreeing thermodynamic functions and temperature dependencies of system components equilibrium partial pressures can be received. Viewing STM as an non-equilibrium, non-stationary system located in non-homogeneous fields of the gradient of energy and concentration, we create a mathematical model in the actual temporal scale. We also develop a method for the numerical calculation of the system of non-linear equation which represent the probable routes of spatial-temporal chemical and phase changes and of kinetic equations of the rate of concentration changes which consider the energy field gradient for each specific system and reactor.

I7.19
IN-SITU ANALYSIS OF GASEOUS SPECIES FOR CVD DIAMOND SYNTHESIS AND THE POSSIBLE REACTION MODEL. Mayu Uede, Yoshiki Takagi, Teikyo Univ of Science & Technology, Yamanashi, JAPAN.

For few years, we had been concentrated of developing completely closed diamond synthesizing system aimed for microgravity experiments. Recently we started the new method with graphite as carbon source. With this method, completely closed system is successfully performed. In-situ gaseous species analyzed with gas chromatographic analysis and possible reaction model will be presented. Graphite rods are used as solid carbon source and at the same time as heater for activate hydrogen gas to hydrogen radicals. Silicon (100) wafers were used for substrates. Hydrogen gas was introduced into the reaction chamber with the suitable initial pressure, and them sealed. Graphite rod was heated and controlled with Joule heating. The deposits were identified with SEM, AFM, XRD and Raman spectrometry. We synthesized diamond with closed system successfully. In this method, a graphite rod was used as a carbon source and a heater, and carbon rod and hydrogen gas were only materials installed in our chamber. With the gas chromatographic analysis data, only methane was observed. Methane was continuously observed while graphite rod was heated up. Pressure was continuously increased because of increasing average temperature of hydrogen gas. 1. Methane, which is believed as major species for diamond synthesis, was identified. 2. Methane was continuously generated in this closed system. We think that these experimental results has revealed the reaction mechanisms on the diamond synthesis for the closed system as follows. Initially installed on the chamber were pure hydrogen and solid carbon only. When carbon source was heated up, hydrogen was activated to hydrogen radicals. Then the radicals reacted with carbon and generated methane. On the substrate, methane generated amorphous carbon and diamond, and hydrogen radicals decomposed amorphous selectively, then were composed to hydrogen molecules. In this manner, without hydrogen consumption, the completely closed system works.

I7.20
A MACROSCOPIC MODEL OF THE GROWTH OF COMPOUND THIN FILMS BY CHEMICAL VAPOR DEPOSITION. Michel Jabbour, Carnegie Mellon University, Dept of Mathematical Sciences, Pittsburgh, PA; Kaushik Bhattacharya, California Institute of Technology, Division of Engineering & Applied Science, Pasadena, CA.

We are interested in the growth of compound thin solid films by CVD. We present a multiphysics macroscopic model that couples the multispecies chemically reacting gas flow to the growing film via the equations governing the morphological evolution of the film-gas interface. The surface is modelled as a separate anisotropic elastic phase, and such phenomena as surface species diffusion, interfacial heat conduction and heterogeneous chemical kinetics are accounted for. In particular, the driving force at the surface is identified, and a thermodynamically consistent growth law is proposed. Specific forms of the growth law are explored using a mesoscopic model that accounts for the terrace-and-ledge morphology of the surface.

I7.21
MODELING OF PVT GROWTH OF BULK SiC CRYSTALS: GENERAL TRENDS AND 2" to 4" REACTOR SCALING. Mark S. Ramm, A.F. Ioffe Physical Technical Inst, Russian Academy of Sciences, St. Petersburg, RUSSIA; Alexei V. Kulik, Igor A. Zhmakin, Sergey Yu. Karpov, Soft-Impact Ltd., St. Petersburg, RUSSIA; Yuri N. Makarov, Univ Erlangen-Nurnberg, Fluid Mechanics Dept, Erlangen, GERMANY.

Coupled heat and mass transport during SiC growth by sublimation technique is modeled to predict temporal evolution of the crystal shape, SiC powder structure, and vapor phase composition in the growth reactor. Both inductively heated graphite and tantalum reactors are analyzed in order to understand the role of chemical transformations on the reactor walls in SiC growth. At every stage of growth a thermoelastic stress distribution due to non-uniform temperature field in the SiC boule grown is computed using the anisotropic elasticity theory. Basing on the stress distribution the density of dislocation arisen from plastic strain relaxation is estimated. Correlation of the dislocation density with the way of SiC seed attachment to a holder is analyzed. Increase of diameter of bulk crystals is one of the most important directions of modern SiC technology. With this respect we simulated scaling of the reactor size to provide the SiC boules of 2" to 4" in diameter. It was found that increase of diameter results in considerable modification of the temperature field in the reactor and, in turn, to suppression of the growth rate. In addition, parasitic deposition of SiC on the reactor walls becomes possible during growth of large-diameter crystals. All these drawbacks have to be improved while designing the 3" and 4" growth systems.

I7.22
A NOVEL LASER-TRIGGERED HOLLOW-CATHODE TRANSIENT PLASMA FOR THIN FILM GROWTH. Prasanna J. Mahawela, Sarath Witanachchi and Pritish Mukherjee, Laboratory for Advanced Materials Science and Technology (LAMSAT), Department of Physics, University of South Florida, Tampa, FL.

We have developed a new vapor deposition method that delivers a highly ionized transient plasma plume of a metallic species in the presence of a low-pressure inert or reactive gas glow discharge. In this process, a transient electrical discharge is formed in a hollow-cathode by a pulse-forming network (PFN) which is triggered by a pulsed CO_2 laser. The presence of the glow discharge is essential for controlled triggering of the plasma. The resulting distributed discharge evaporates the metallic anode placed inside the cathode tube to produce a highly excited and ionized plasma plume that leads to defect-free film growth. In this paper, we report the application of this technique to the growth of diamond-like carbon (DLC) and C-N films using carbon electrodes in an Ar or N_2 ambient, respectively. A high density of ions, in conjunction with the high kinetic energies imparted to carbon ions by substrate biasing promoted the formation of the sp3-bonded DLC phase, and enhanced reactivity with nitrogen to form carbon nitride. Films that are uniform over a large area with deposition rates exceeding 30$\AA$ per discharge pulse have been grown. The ionic content of the plasma, spatial distribution of ions, and plume expansion dynamics as investigated by time-of-flight ion probe measurements, optical emission spectroscopy and CCD imaging will be presented. This work is supported in part by the National Science Foundation (Grant No. DMI-9622114) and the US Department of Energy (Grant No. DE-FG02-96ER12199).

I7.23
SYNTHESIS AND CHARACTERIZATION OF α-ALUMINA FILMS VIA COMBUSTION CHEMICAL VAPOR DEPOSITION. G. Grandinetti[1], S. Shanmugham[2], J.M. Hampikian[1], M.R. Hendrick2 and H.A. Luten[2]. [1]School of Material Science and Engineering, Georgia Institute of Technology, Atlanta, GA, [2]MicroCoating Technologies, Chamblee, GA.

α-Alumina films are useful for high-temperature, wear, and semiconductor device applications because of the good oxidation resistance, hardness, and excellent electrical properties of alumina. α-Alumina films have been previously synthesized using techniques such as chemical vapor deposition, sol-gel, physical vapor deposition,

and plasma spraying. This paper will present an alternative approach for producing high quality dense α-alumina coatings using a flame-assisted process called combustion chemical vapor deposition (CCVD). This process is an open atmosphere, vapor deposition technique that does not require the use of a reaction chamber. In this work α-alumina films were grown on YSZ, Ni-20Cr and INCO625 and characterized by SEM and XRD. The high temperature oxidation behavior of α-alumina on Ni-20Cr is characterized at temperatures between 800 and 1200.