Manufacturing Science and Technology Group
Room 611 - Session MS-MoM

Advanced Design Methodologies and Factory Modeling

Moderator: S. Rauf, Motorola Inc.

8:40am **MS-MoM2 Aspect Ratio Dependent Etching***, **T.S. Cale**, M. Bloomfield, S. Soukane,* Rensselaer Polytechnic Institute

This presentation reviews a study of 'aspect ratio dependent etching' (ARDE); i.e., the effect of aspect ratio on etch rate in reactive ion etching (RIE) systems. The goal is to provide guidelines for etch process developers, and involve simple but flexible models for the transport and kinetics. EVOLVE, a deposition, etch and thin film flow simulator, is used to characterize the ARDE via an RIE 'lag parameter'. Further simulation is then used relate ARDE to the neutral-to-ion flux flux ratio, in the simplified transport and kinetic models. This flux ration ratio can be related to RIE operating conditions.

9:00am **MS-MoM3 SEMATECH's Plasma Modeling Project***, **G.L. Bell**, P.M. Ryan,* Oak Ridge National Laboratory **INVITED**

As wafer costs increase with size, the expenses associated with developing new tools and running process development experiments increase prohibitively. Robust plasma models and high-performance simulation tools are needed to reduce the significant cost of introducing new processing technologies. The goal of the SEMATECH Plasma Model Development project is to accelerate technology development through the advancement of predictive models for plasma etching. Three major barriers must be overcome to accomplish this goal: 1) the lack of detailed verified data on actual production tools to be used for testing the models and to support process development, 2) the need for gas phase and surface mechanisms for commercially relevant oxide and metal etch plasmas, and 3) the absence of a comprehensive database of detailed cross-sections of plasma etching gases for use by the modeling community. To address these hurdles, this SEMATECH project combines the efforts of universities and national labs into an integrated modeling effort. Supported research includes development of a relevant gas phase chemistry database through cross-section and reaction rate measurements and computations, development of surface reaction mechanisms from particle beam and in situ surface measurements during plasma processing, and experimental measurement of plasma parameters and ion/neutral species distributions on representative plasma reactors. The team produces "best known" database sets (gas phase, surface reactions, plasma diagnostics data and model inputs) to develop physical models for input into advanced codes which predict etch rate (selectivity) and uniformity. This presentation outlines the project structure, the role of the working groups and some representative data obtained to date. @FootnoteText@ G.L. Bell is currently on assignment to SEMATECH's Interconnect Division.

9:40am **MS-MoM5 A Comparison of Spectroscopic Measurements of an Inductive Plasma Source with the INDUCT Model***, **M.L. Huebschman**, J.G. Ekerdt,* University of Texas, Austin*; P.A. Vitello,* Lawrence Livermore National Laboratory*; J.C. Wiley,* University of Texas, Austin

Noninvasive spectroscopic measurements of an inductively driven hydrogen plasma source with density and temperature characteristic of plasma processing tools have been done with an ultimate application of cleaning of silicon substrates These measurements allow full radial and axial profiles of electron density and temperature to be measured from absolutely calibrated multichannel spectroscopic measurements of upper state number densities and a collisional radiative model. Profiles were obtained over a range of powers from 50 to 200 W and pressures from 5 to 50 mtorr in hydrogen in a small cylindrical source. The hydrogen working gas and simple cylindrical geometry was chose to simplify detailed comparisons with a 2D computational model (INDUCT95) which uses a fluid approximation for the plasma and neutral gas. The code calculates the inductive coupling of the 13.56 MHz RF source, the collisional, radiative, and wall losses as well as a complete chemistry model for H@sub 2@, H, H@super +@, H@sub 2@@super +@ and H@sub 3@@super +@. We found good agreement between the model and experimental data over part of the operational range. Ranges of agreement and divergence will be discussed.

10:00am **MS-MoM6 Characterization of Showerhead Performance at Low Pressure***, **D.B. Hash**,* ELORET*; T. Mihopoulos,* Motorola Inc.*; M. Meyyappan,* NASA Ames Research Center*; D.G. Coronell,* Motorola Inc.

The overall objective of this work is to characterize the flow through showerheads by deriving pressure drop versus velocity correlations that can be then used in reactor scale simulations where the showerhead is approximated as a porous medium. At relatively low Reynolds numbers (< 1-10 based on the hole length scale) and in the absence of slip flow, Darcy's Law, gradient P = µ U/ k, can be used to express the relation between the pressure drop and velocity where µ is the fluid viscosity and k is the permeability that can be theoretically predicted as k = e R@super 2@ /8, where e is the porosity. However, at sufficiently small hole diameters and decreased pressures (< 5 Torr), the Knudsen number based on showerhead tube radius increases, and the flow may be in a transition regime. Different expressions have been proposed to account for this effect in the permeability by expressing k as a function of either pressure or Knudsen number. But at even higher Knudsen numbers, the pressure drop - velocity dependence is non-linear, and Darcy's Law no longer holds such that a permeability cannot be defined. The direct simulation Monte Carlo method is used along side conventional CFD techniques to determine the extent to which the CFD technique is appropriate and helps to derive correlations for the more rarefied cases of interest in these showerhead flows.

10:20am **MS-MoM7 IMP-PVD Equipment Level Process Analysis Using Simulation***, **P.L.G. Ventzek**, S. Rauf, D.G. Coronell, V. Arunachalam, X.-Y. Liu, J. Arnold, D. Denning, S. Garcia, A. Korkin,* Motorola Inc.*; Y.-K. Kim,* National Institute of Standards and Technology

Ionized metal plasma physical vapor deposition continues to be viewed as a promising means of depositing seed and barrier layers in tight critical dimension high aspect ratio features. Issues that require attention at the equipment level deal with obtaining sufficient film continuity and conformality in a uniform way across a wafer. Critical to these metrics are the delivery of the appropriate net ion current (both metal and inert) and ionization fraction of the metal flux (energy distribution and angular spread). Also important may be the energy content brought to the surface by excited state species. We have characterized these parameters using HPEM (University of Illinois) and will present a comparison between the model predictions for DOE's performed on a Cu IMP-PVD chamber. Of note from this study is the sensitivity of predicted behavior on the capacitive-inductive power distribution from the inductive coils. Very high percentages of the power delivered to the coil are lost capacitively and the fraction in very sensitive to the power capacitively coupled to the wafer. The role of metastable species generated in the plasma is also investigated. Metastable species are usually thought only to play the role of facilitating relatively low energy pathways for ionization . It turns out that heavier metals have a wealth of metastable states even at very low energy allowing them to alter the plasma behavior and to facilitate different processes at the surface when compared to lighter atomic number metals.

10:40am **MS-MoM8 Holistic Yield Learning Methodology***, **A.J. Strojwas**,* PDF Solutions Inc. **INVITED**

Each year, IC manufacturers invest billions of dollars in new equipment in an attempt to increase their competitiveness by delivering enhanced performance and more functionality at a lower cost. Success in today's marketplace requires successful technology integration under increasing market pressure to deliver products as quickly as possible. Unfortunately, standard yield improvement practices focus too narrowly on defect elimination and use techniques that solve yesterday's not today's problems a comprehensive view of yield learning. To ensure profitability, a new approach to yield learning must be developed. Inevitably, these changes require a re-defining of the interfaces between design, test and manufacturing. In this paper, we present a comprehensive view of the yield problem and a "holistic" yield ramping methodology specifically designed to significantly reduce the yield ramp time by eliminating not only defects, but also by resolving parametric and systematic problems. Manufacturing defect data, process recipe, and design information are analyzed simultaneously, to derive a much deeper understanding and subsequent solution to the process and design architecture issues that affect yield and performance. In combination with the use of simulation and a hypothesis-driven work style, this approach delivers increased yield and performance in a fraction of the time required by traditional methods.

11:20am **MS-MoM10 Particle Simulations of Chemically Reacting Plasmas***, **M.A. Gallis**, T.J. Bartel,* Sandia National Laboratories

This work focuses on the development of a particle simulation code that can be used for the modeling of low pressure inductively coupled high density plasma reactors. The code is based on the Direct Simulation Monte Carlo methodology where a relatively small number of particle simulators mimic the behavior of a large number of real particles. Only heavy particles (ions and molecules) are directly modelled. The electron number density is deduced from this of the ions assuming local charge neutrality. Since the plasma sheathes are very small the assumption of charge neutrality is used through out the computational domain. The electron temperature is calculated using two different methods. The first one uses an electron energy equation using ICP power electron conduction and inelastic electron impact reactions. The second one uses a kinetic treatment of the electrons creating an equilibrium distribution of electrons every time an estimation of the electron temperature is needed. The motion of the electron gas is then followed in a fully kinetic fashion and for a time period short enough to assume that the heavy particles remain in their positions. The ICP power deposition for both methods is determined by an external code from Oakridge National Laboratories, ORMAX. The neutral-neutral and neutral ion interactions are directly modeled. The two methods will be compared for two electro-negative systems; pure CL2 and C2F6 in the GEC test cell geometry.

11:40am **MS-MoM11 Simulations of Low Field Helicon Discharges@footnote 1@***, **R.L. Kinder**, M.J. Kushner,* University of Illinois, Urbana

Due to their high ionization efficiency, ability to deposit power within the volume of the plasma and ability to operate at low pressures, helicon reactors are attractive for downstream etching and deposition. The power coupling of the antenna radiation to the plasma is a concern due to issues related to process uniformity when using high magnetic fields (100s G to kG). Operating at low magnetic fields (< 100 G) is therefore preferred to provide more uniform ion fluxes and to reduce the cost of the tool. To investigate helicon operation over large ranges of magnetic fields a full tensor conductivity has been incorporated into the electromagnetics module of the Hybrid Plasma Equipment model (HPEM) augmented by an effective collison frequency to account for Landau damping. Plasma properties for helicon excitation of Ar, Ar/N@sub 2@ and process relevant gases (CF@sub 4@, C@sub 2@F@sub 6@) as a function of magnetic field strength, field configuration and power will be discussed. Results of an argon plasma excited by a m = 0 mode field operating at 13.65 MHz shows a resonant peak in the plasma density occuring in the low magnetic field range and is attributed to off-resonant cyclotron heating. The transition from inductive coupling to helicon mode appears to occur when the fraction of power deposited through radial and axial fields dominates. Results from HPEM-3D will be used to resolve helicon wave structure in the m = 1 and -1 modes. @FootnoteText@ @footnote 1@This work was supported by SRC, AFOSR/DARPA, Applied Materials and LAM Research.

Manufacturing Science and Technology Group
Room 611 - Session MS-MoA

Ultra-Clean Society and Contamination Free Manufacturing

Moderator: A.C. Diebold, Sematech

2:00pm **MS-MoA1 Highly Reliable Ultra Thin Gate Oxide Grown using Water Vapor Generator***, **O. Nakamura**, T. Ohkawa, M. Nakagawa, Y. Shirai,* Tohoku University, Japan*; K. Kawada, N. Ikeda, Y. Minami, A. Morimoto,* Fujikin Incorporated, Japan*; T. Ohmi,* Tohoku University, Japan **INVITED**

High-reliability ultra thin oxide film is required for future ULSI manufacturing, where perfect uniformity and very high yield in volume production of large diameter wafers era must be guaranteed. In case of wet oxidation, water vapor is most commonly generated by burning H@sub 2@ in O@sub 2@ ambient. So, this torch-type has a potential problem of particle contamination of the water due to the micro-powder from the quartz combustion nozzle. In order to obtain wet ambient without contamination, we have developed a new Water Vapor Generator (WVG) using catalytic reactor. Additionally, the WVG can generate H2O from the vacuum to the high-pressure condition. This WVG is expected to be used in various processes where water vapor is needed.In this presentation, we will demonstrate a new gate oxidation process to form high-reliability ultra thin gate oxide at low temperature with highly concentrated H@sub 2@O using WVG system. For example, for substrate injection, the 50% Q@sub BD@ values of conventional dry oxides (900@super o@C) and advanced wet oxides formed at the low temperature using highly concentrated moisture (90% H@sub 2@O/Ar, 750@super o@C) are 9.5 C/cm@super 2@ and 70 C/cm@super 2@, respectively. For gate injection, the 50% Q@sub BD@ values of conventional oxides and advanced oxides are 6.5 C/cm@super 2@ and 25 C/cm@super 2@, respectively. Moreover, we will discuss the influence of oxidation ambiences such as surplus O@sub 2@ and H@sub 2@ ambience and oxidation temperature for electrical characteristics. In conclusion, ultra thin gate oxide using WVG has high breakdown strength under electrical stress. A newly developed oxidation is effective to grow a tunnel oxide for flash memory, which is operated under high electric field.

2:40pm **MS-MoA3 High-integrity Ultra-thin Silicon Nitride Film Grown by Plasma Nitridation of Silicon Surface at Low-temperature for Giga Scale Devices***, **K. Sekine**, Y. Saito, M. Hirayama, T. Ohmi,* Tohoku University, Japan

The progress of MOSLSI technology has been based on the shrinking of MOSFET's. Along with downsizing MOSFET's for more than 25 years, the gate oxide equivalent thickness of MOSFET's has continued to be reduced. Since the invention of MOS device, thermally grown silicon oxide, the prevailing gate dielectric for Si based MOS devices, processes remarkable electrical properties that are unmatched by other materials. However, transistor scaling is driving gate oxide equivalent thickness to 3 nm and below, when direct tunneling current becomes significant. Ultra thin silicon oxide below 3 nm is not expected to be robust enough for future transistor gate dielectric application. In order to continue downsizing MOSFET's, thermally grown silicon oxide will be replaced by higher dielectric-constant films, for example Ta@sub 2@O@sub 5@ and Si@sub 3@N@sub 4@. A radial line slot antenna (RLSA) high-density plasma system can form high-integrity silicon nitride film at a temperature of 400 °C. We focus attention on electrical properties of ultra-thin silicon nitride films grown by radial line slot antenna high-density plasma system at a temperature of 400°C as an advanced gate dielectric film. The results show low density of interface trap and bulk charge, lower leakage current than jet vapor deposition silicon nitride and thermally grown silicon oxide with same equivalent oxide thickness. Furthermore, they represent high breakdown field intensity, almost no stress-induced leakage current, very little trap generation even in high-field stress, and excellent resistance to boron penetration and oxidation.

3:00pm **MS-MoA4 Generation of Positively Charged Particles at an Anode and Transport to Device-wafers in a Real rf-plasma Etching Chamber for Tungsten Etch-back Process***, **T. Moriya**, N. Ito, F. Uesugi,* NEC Corporation, Japan*; Y. Hayashi, K. Okamura,* NEC Kyushu, Ltd., Japan

In this paper, it is clarified that the particles, flaked off from a grounded anode of parallel-plate rf plasma etching equipment, have positive charges. Moreover, the particles transport from the anode to the device-wafer on the cathode with keeping away from bulk plasma. In previous papers, we have reported that, in the middle space between the two electrodes, many particles were observed at the timing of the rf power off, and seemed to be drawn to the wafer with the residual negative self-bias voltage.@footnote 1,2@ To clarify the polarity of charge and the transport path of particles, the appearances and the trajectories in relation to the workings of the etching equipment are studied in detail both near the anode and the device-wafer on the cathode. Surprising results are obtained. Near the grounded anode, a few particles appear constantly and have parabolic trajectories with open upward in the duration of rf power, and many particles appear and have sharply curved trajectories from the anode to the chamber wall at the rf power off. On the other hand, near the wafer on the cathode, almost all particles appear at the rf power off and are drawn from the chamber wall to the wafer. These results mean the particles are reflected by the plasma potential, and they transport from the anode to the wafer with keeping away from the residual bulk plasma under the existence of attractive force between the particles' positive charge and the residual negative charge of the wafer. @FootnoteText@ @footnote 1@F. Uesugi, et al., J. Vac. Sci. Technol. A 16, 1189 (1998).@footnote 2@N. Ito, et al., J. Vac. Sci. Technol. B 16, 3339 (1998).

3:20pm **MS-MoA5 Standardization of the Method to a Moisture Concentration in Hydrogen Chloride Gas with Diode Laser Absorption Spectrometry***, **Y. Ishihara**,* UC Standardization Committee, Japan*; Y. Sakakibara,* NTT Advance Technology Corporation, Japan*; Y. Kunii,* Kokusai Electric Co., Ltd., Japan*; K. Hasumi,* Hitachi Tokyo Electronics Co., Ltd., Japan*; I. Matsuda,* Showa Denko K.K., Japan*; N. Miki,* Ultraclean Technology Research Institute, Japan*; A. Ohki,* Oosaka Sanso Kogyo Ltd., Japan*; Y. Shirai,* Tohoku University, Japan

A standard method is proposed, using diode LASER absorption spectroscopy, to measure the moisture (H@sub 2@O) in hydrogen chloride (HCl) gas at concentrations between 100 ppb to 0.1%. This standard is laid down to measure trace H@sub 2@O in HCl at point of use. In this standard, HCl with H@sub 2@O of unknown concentration (sample gas) is introduced into a laser absorption spectrometer which is kept at reduced pressure. Measurement is performed in the range of 1370 nm to 1389 nm in wavelength, and the second-derivative absorption intensity of H@sub 2@O is calculated. Using the second-derivative absorption intensity and pre-defined calibration curve, the H@sub 2@O concentration is determined. The determination limit, which was defined as 3 times of the standard deviation of the second-derivative intensity, was found to be 100 ppb when a program for noise cancellation was employed. For verification of calibration curve, calibration curves which were prepared at different timings at different places by different people showed good agreement of over 95%. Moreover, it is proved that calibration curve of H@sub 2@O in HCl can be substituted by that of H@sub 2@O in N@sub 2@ which is corrected with a correction coefficient.

3:40pm **MS-MoA6 Gas Distribution System Using an Advanced Flow Controller***, **M. Nagase**, O. Nakamura, M. Kitano, Y. Shirai, T. Ohmi,* Tohoku University, Japan

In a single wafer treatment, an individual process is carried out within 30-40 sec. And an accurate control of the working pressure and composition ratio of all source-gases in the process chamber through the entire process period is essentially required for establishing high quality processes. We have developed a total gas system combining a distribution system and a pumping system in order to satisfy this requirement and the system evaluated using FT-IR method. The gas distribution system consists of an advanced flow controller(FCS) and an electrically controlled valve(ECV). The FCS is introduced into the principal that the flow rate is directly proportional to the upstream pressure when the upstream pressure of a orifice is two times higher than the downstream pressure. The advanced distribution system using the FCS and the ECV does not observe overshoot phenomena and so stable gas flow rate can be distributed in the chamber after valve operation. However, in the case of combination chamber volume and gas flow rate, it occurred time lag to become stable gas concentration in chamber. To solve this problem, we developed the multi-step flow rate control. Consequentially, the working pressure rises momentarily because more gas distributes than steady state gas flow rate. This problem is solved to control the pumping property by changing the purge gas flow rate which supplying into the drug screw pump with the FCS. Combining the advanced gas distribution system using the FCS and the ECV and the pumping system, we can perfectly control process parameters such as gas composition and the working pressure on the moment.

4:00pm **MS-MoA7 Investigating Molecular Contamination in Cleanrooms***, **P.H. Schnabel**, G. Goodman,* Charles Evans & Associates*; D. Nehrkorn, M. Kendall,* Surface Science Laboratories*; G. Strossman, P. Lindley,* Charles Evans & Associates

As the line widths of microelectronic devices approach 0.1 micron, the presence of airborne molecular contamination (AMC) in fabs and cleanrooms has become a major concern for the semiconductor industry. In order to achieve low defect rates in these next generation devices the technical ability to identify, isolate and eliminate AMC is a substantial challenge. AMC can potentially result from every material within a cleanroom or a fab but the main sources for AMC are process chemicals, construction materials and the local environment. AMC defects can cause changes in the wafer's electrical properties, uncontrolled boron or phosphorous doping, etch rate shifts, threshold voltage shifts, wafer and stepper optics hazing and high contact resistance. In this study we demonstrate that TOF-SIMS can be utilized for identifying different types of condensable airborne contaminants and for monitoring those contaminants in cleanrooms. For this purpose witness wafers were placed in a newly constructed class 10 cleanroom and analyzed periodically over a time of 6 months. In order to identify potential sources of AMC the ougassing of individual materials that are typically present in cleanrooms was studied by TOF-SIMS, GCMS and FTIR. The materials under investigation include cleanroom construction materials (e.g. floor tiles, filters, sealant etc.), cleanroom furniture, cleanroom garments and cleanroom utensils. In these experiments each of the materials 'delivers' a fingerprint which can be used to identify potential sources of cleanroom contamination. The transfer of contaminants onto silicon wafers that are brought in contact with these materials was studied as well. The long term objective of this part of our studies is to generate an extensive database which allows us to link the observed contaminants on wafers with potential sources within the cleanroom environment. Both, transfer through the gas phase and by contact will be evaluated.

4:20pm **MS-MoA8 Minimizing Particle Generating Contamination in Polysilicon LPCVD***, **J. Krueger**,* Texas Instruments Incorporated*; J. Snow, J. Hardin, J. Gratz,* Millipore Corporation

Increasing wafer size and decreasing critical dimensions exacerbate the chances of a particle coming to rest in a die-killing location. In this study, the effect of point-of-use (POU) purification was evaluated by processing two sets of split lot wafers on an LPCVD polysilicon horizontal furnace. The gas quality downstream of the furnace was evaluated using a closed ion source (CIS) residual gas analyzer (RGA) and an in-situ particle counter (ISPM). Wafer particle counts, film contamination levels by secondary ion mass spectroscopy (SIMS), surface roughness and grain size measurements by atomic force microscopy (AFM) were all used to compare the split lot halves processed with and without purification. SIMS analysis showed that oxygen levels in the film were lower for wafers run with the purifiers. Also, secondary ion counts of silicon were slightly higher in the film of the wafers processed with the purifiers. Wafer particle data showed that wafers run with the purifiers had 72% fewer added defects. The ISPM sensor showed that there were 37% fewer particles with the purifiers in place. RGA results revealed lower moisture levels with the purified silane deposition step compared to unpurified.

4:40pm **MS-MoA9 Highly Concentrated Ozone Gas Supplied at Atmospheric Pressure Condition as a New Oxidizing Reagent for the Formation of SiO@sub 2@ Thin Film on Si***, **K. Koike**,* Iwatani International Corporation, Japan*; S. Ichimura, A. Kurokawa, K. Nakamura,* Electrotechnical Laboratory, Japan

Ozone is expected to be one of promising oxidizing reagents for the fabrication of future ULSI device. We have investigated ozone oxidation on Si(100) substrate with high purity (about 80 vol%) ozone gas, and have revealed various merits of ozone oxidation; e.g., ozone can form dense SiO@sub 2@ film on a Si substrate at lower substrate temperature than that used at a conventional thermal oxidation process, ozone can oxidize hydrogen-terminated silicon surface which oxygen molecules cannot, etc.@footnote 1,2@ One major problem which has to be solved before the ozone oxidation is applied to a practical process is low oxidation rate. Since the pressure of the high purity ozone gas was low (typically; <10@super -4@ Pa), only 2 nm thick SiO@sub 2@ film could grow on a Si(100) substrate by 2 hours ozone gas exposure at a substrate temperature of 973K. In the present study, we report that the problem could be solved by fabricating another type of ozone generator. The generator can supply highly concentrated ozone gas at atmospheric pressure condition, by desorbing ozone from silica-gel on which ozone/oxygen mixture gas had been adsorbed at lower temperature. Ozone concentration in the gas from the generator can be changed between 0 and 70 vol%, by controlling the ozone adsorption and desorption condition. Even with 25 vol% ozone gas, it was confirmed that SiO@sub 2@ film as thick as 3.3 nm grew on a Si (100) wafer kept at 648 K by 30 min exposure. The wafer had chemical oxide film (thickness; 1.2 nm) before the ozone oxidation. So SiO@sub 2@ film with thickness of 2.1 nm could be additionally formed with the ozone gas, while under the same experimental condition only 0.6 nm thick SiO@sub 2@ film could be formed on the same wafer with pure oxygen. It should be emphasized that the density of the SiO@sub 2@ film formed with 25 vol% ozone gas was equivalent to the density of a film formed by a thermal oxidation process at 1023K, judging from their etching rates with dilute HF solution. The result suggests that the present ozone oxidation process has high possibility to be adopted as a new process for Si oxidation. The details and performance of the new ozone generator are presented together with the dependence of the oxidation of Si(100) on ozone concentration and on Si substrate temperature. @FootnoteText@ @footnote 1@ A. Kurokawa, S. Ichimura, and D.W. Moon, Mat. Res. Soc. Symp. Proc. 477, 359 (1997). @footnote 2@ A. Kurokawa, K. Nakamura, and S.Ichimura, Mat. Res. Soc. Symp. Proc. 513, 37 (1998).

5:00pm **MS-MoA10 A Comparison of VPD, TXRF, and Surface SIMS to Detect Fe, Ni, Cu, and Al on Silicon Wafers***, **V.K.F. Chia**, J. Metz, M.J. Edgell,* Charles Evans & Associates

The emphasis on contamination free manufacturing (CFM) continues within the manufacturing environment through the use of cleanrooms and the practice of contamination-free procedures. Stringent contamination limits for polished and epitxial substrates and surface preparation (i.e. before gate oxide growth) are suggested by the National Technology Roadmap for Semiconductors (NTRS). Today's requirement for surface metals is typically in the range of 10@super 10@ at/cm@super 2@. Future needs are anticipated to be in the mid-10@super 9@ at/cm@super 2@. The transition metals Fe, Ni, and Cu are considered to be very damaging at the gate oxide level, and therefore requirements for these are becoming more stringent. Al is important to monitor because at concentrations below 10@super 11@ at/cm@super 2@ it can increase the oxide growth in the very thin gate oxide regime. This is a different effect compared to higher levels of Al (e.g. >10@super 12@ at/cm@super 2@), which decreases gate oxide thickness for thicker gate oxides. VPD, TXRF and SurfaceSIMS are commonly used in surface clean technology. VPD is a collection/scanning procedure that concentrates the metal contaminants on a wafer surface into a droplet. VPD procedure is popular because it improves the detection limit of the final analytical measurement technique. TXRF is well established as a surface sensitive technique. It can detect medium- and high-Z elements (sulfur to uranium) on silicon wafers at very low concentration levels. Routine detection limit is approximately 10@super 10@ at/cm@super 2@ or better. SurfaceSIMS is a powerful analytical technique for substrate engineering. Typical detection limit of this technique is 10@super 8@ to 10@super 10@ at/cm@super 2@. SurfaceSIMS complements TXRF by detecting low-Z elements, such as Li, Na, K, and Al. This presentation provides an overview of VPD, TXRF, and SurfaceSIMS and their application to detect Fe, Ni, Cu, and Al.

Manufacturing Science and Technology Group
Room 611 - Session MS-TuM

New Manufacturing Research Paradigms

Moderator: C.B. Whitman, CVC Products Inc.

8:20am **MS-TuM1 Proposal of New Paradigm LSI Structures and Their Manufacturing**, ***T. Ohmi***, *M. Hirayama, Y. Shirai,* Tohoku University, Japan **INVITED**

UCS (Ultra Clean Society) was established in October, 1988 and is going to finish its mission at the end of September, 2000. For these 11 years, UCS has developed many new technologies mainly focussing on an improvement of process quality by removing unknown factors from manufacturing such as contaminants (particles, metals, organic molecules, moisture molecules, native oxides, surface micro-roughness, electrostatic charge-up and etc.) and fluctuations of process parameters giving an influence on process results. Consequently, semiconductor processes can be understood in a scientific manner, resulting in an improvement of process reproducibility. Developments of very well regulated high density plasma source for RIE, sputtering and plasma CVD, and room temperature 4 steps substrate surface cleaning have drastically improved process quality and process reproducibility. Equipment individuality has been overcame by introducing RF circuit specification to the process chamber and very well regulated process gas supply to the wafer surface by newly developed Flow Control System, so that so that process recipe can be applied to all other identical process chambers resulting in a complete process reproducibility and a low price process equipment. Right now, very high throughput and very compact manufacturing line must be established having a capability of simplified process steps, very low consumption volume of electricity and resource materials down to 1/10. Complete process reproducibility will make it true the computer simulation of all processes by microprocessors. Process flow and process conditions will be derived by computer simulation just after the completion of LSI design. Manufacturing of newly designed LSI will start immediately without using pilot wafers. Very low cost and very QTAT manufacturing are crucial for coming networked digital home electronics era. New society will focus on these issues.

9:00am **MS-TuM3 The IC Interconnect Millenium Transitions; Al to Cu, SiO@sub 2@ to Low-K**, ***K.A. Monnig***, *A.C. Diebold,* SEMATECH **INVITED**

This paper will give a general overview of the transitions occurring in I.C. interconnect systems today; Al conductors with SiO@sub 2@ insulators are planned to be supplanted by Cu metal with Low-K dielectrics. The reasons why this transition is happening now will be outlined. Almost all of the fabrication processes used will be changed and these differences will be reviewed. Special attention will be given to vacuum processing applications that will be lost due to the changes and to the new opportunities created. An assessment of financial and technical risks will be shown. Finally a current status report on the progress of the various transitions will be presented.

9:40am **MS-TuM5 Cooperative University Research for Critical Front End IC Processes**, ***J.R. Hauser,*** North Carolina State University **INVITED**

MOS device physics and technology are rapidly approaching some fundamental limits as device dimensions are scaled below 100 nm. Fundamental tunneling limits to SiO2 gate oxide are approaching as oxide thickness scales below 2 nm. Low resistance source/drain contacts are becoming increasingly difficult as junction depths decrease and required doping densities approach or exceed solid solubility limits. In order to address these issues, a new cooperative research center was established in 1998, the SRC/SEMATECH Front End Processes Research Center. The Center seeks to bring together research in three areas: (a) Fundamental materials and interface physics and chemistry, (b) Process integration and demonstration and (c) Rapid transfer of technology to industry and equipment companies. To effectively integrate such research efforts, requires new paradigms for cooperative university research and this presentation will discuss how this is being approached within the SRC/SEMATECH Research Center.

10:20am **MS-TuM7 Industrial-Academic-Government Partnerships; A Successful Example**, ***J.B. Bindell,*** Cirent Semiconductor (Lucent Technologies) **INVITED**

Semiconductor manufacturers have always had a close relationship to Universities, using them for purposes ranging from professional training to contract research and development. These relationships have also been synergistic, with the Universities strongly benefiting from in depth relationships with high technology firms. These reverse benefits have also been multifaceted, with funding, training delivery opportunities and contact with well known industrial scientists yielding many productive interactions. When Lucent Technologies located its leading edge manufacturing facility in Orlando, Florida, and then moved a major Bell Labs R&D division to the same facility, a number of interactions were suddenly spawned. Three distinct players were involved. These were Lucent, which found itself in need of strong University support, the University of Central Florida (UCF) and the University of South Florida (USF), both relatively close neighbors, and the state of Florida itself which had designated an extended area between Orlando and Tampa as the "Florida High Tech Corridor". The corridor's establishment was an important part of a desire to make this region a magnet for additional semiconductor manufacturers and for the economic growth that would surely follow. This three-way partnership between industry, government and education has led to a new paradigm for such interactions in which the boundary between our industrial laboratory and those of the Universities has become unclear. In fact, in the disciplines where Lucent has needed University support, these partnerships have created resources which are well on their way to national prominence. This presentation will center on the University programs and facilities that have developed from this partnership as well as on the issues of industrial involvement in the area of workforce development.

11:00am **MS-TuM9 Cooperative Research on Environmentally Benign Semiconductor Manufacturing**, ***F. Shadman,*** NSF/SRC Engineering Research Center **INVITED**

This presentation will be an overview of the multi-disciplinary research program at the NSF/SRC Engineering Research Center involving a team of researchers from six universities. The Center is focusing on a dual approach to the environmentally benign semiconductor manufacturing. The first approach involves the development of novel processes where environmental, safety, and health (ESH) factors are among the primary design parameters together with performance and cost. The second approach focuses on improving the existing processes for ESH gain. Several examples of the thrust areas and projects of the Center will be discussed. In particular, the following topics will be covered in depth: Reduction of water and chemical usage for surface preparation and wafer cleaning; Environmental gains in the development of new low-k materials/processes as well as the new etch and deposition methods; Waste reduction and recycling in the CMP process; Energy use reduction through novel purification processes; Application of simulation and integrated modeling for recycle and reuse optimization in selected fab processes. Finally, the educational program of the Center that focuses on including the ESH subject in the core engineering curriculum will be discussed briefly.

11:40am **MS-TuM11 EquiPSim: Hands-On Training in Semiconductor Equipment and Process Behavior**, *A.R. Rose,* ***G.W. Rubloff,*** *N. Kositsyna, N. Gupta, R. Sreenivasan, W.S. Levine,* University of Maryland

We have developed EquiPSim (Equipment and Process Simulation), a software-based learning system for semiconductor manufacturing aimed at providing active hands-on experience in the equipment and process environment of semiconductor manufacturing. Physically-based dynamic simulators, validated against experiment, were constructed on a commercial PC-based simulation software platform (VisSim@super TM@ v/3) and linked to a graphical user interface built on a Delphi@super TM@ v/4 visual development platform. As the learner operates the controls (actuators such as valves, settings, etc.) on the equipment or changes system design variables, system responds realistically and accurately in real time, allowing the user to explore system behavior freely and to carry out open-ended learning exercises. A host of user-controllable tools are also provided to present a rich learning environment, including: guidance, reference, and exercise materials in hypertext, accessed locally or over the Internet; active links between the guidance materials and the visual representation of the system; tools for modifying system design parameters; a lab notebook for recording design parameter and experimental results; and tools to enable distance collaboration. The software architecture is structured to facilitate separable authoring, in which the domain expert need concentrate only on the physical fidelity of the simulator and the guidance concepts to be taught, while the user interface is built from templates and predefined application objects by someone with modest software skills. Modules covering vacuum and gas flow technology, heat transfer mechanisms, and chemical reaction processes are aimed at novices, while modules in process control and optimization strategies are aimed at more experienced learners. The presentation will feature a live demonstration. Further information is available at the Center for Engineered Learning Systems (CELS) website at /www.isr.umd.edu/CELS/.

Manufacturing Science and Technology Group
Room 611 - Session MS-TuA

Interconnect and Integration

Moderator: S. Shankar, Intel, Inc.

2:00pm **MS-TuA1 CD Control Optimization Methodology on Shallow Trench Isolation Substrate for Sub-0.25µm Technology Gate Patterning***, M.H. Fan,* ***H. Gerung****, P. Yelehanka, A. Cheng, M.S. Zhou, C. Chi,* Chartered Semiconductor Manufacturing Ltd., Singapore*; C.H. Tan, J. Xie,* Institute of Microelectronics, Singapore

The impact of post-Shallow Trench Isolation (STI) Chemical Mechanical Polishing (CMP) on gate critical dimension (CD) control for submicron technology had been studied. The response of the gate CD depends upon STI process scheme whether it is recess (STI lower than active) or elevated (STI higher than active). Two subjects had been studied: first, CD uniformity as the function of STI step height with active and secondly, CD uniformity as the function of the size of the active area. The topology step height and active size affect the resist coating and organic BARC thickness uniformity. BARC thickness uniformity affects the substrate reflectivity, which leads to variation in the effective exposure dose. This dose variation leads to CD swing across the wafer and resulting in non-uniform CD. We used AFM surface scan to study the topographical variations caused by CMP process on different active area size. A new simulation technique using topographical swing curves and CD error contour plot was applied in this work to optimize BARC and resist thickness. Prolith/2 from FINLE was used for process simulation and excellent agreement was found between simulation and experimental results. Better CD control can be achieved by avoiding extreme recessed or elevated STI topology.

2:20pm **MS-TuA2 Patterning of Xerogel in High Density Fluorocarbon Plasmas***,* ***T.E.F.M. Standaert****,* State University of New York at Albany*; C. Hedlund,* Uppsala University, Sweden*; E. Joseph, G.S. Oehrlein,* State University of New York at Albany*; W.N. Gill, P.C. Wayner, J.L. Plawsky,* Rensselaer Polytechnic Institute

The upcoming generations of integrated circuits will employ low dielectric constant (k) materials as interconnect isolation. Compared to conventional oxides, low k materials contribute less to circuit delays. Porous spin-on-glasses (k<2.5), e.g. Xerogel, are of particular interest for high speed devices. We present a detailed study on the patterning of Xerogel films with a porosity varying from 64% to 83%. The films were etched in a high density plasma tool using fluorocarbon gases. This allows for a high etch rate. For example, the etch rates in a CHF@sub 3@ discharge of a 78 % porous Xerogel film and a thermal oxide film are 2750 and 400 nm/min, respectively. The high etch rates can only partially be explained by the porosity of the films. Namely, the etch yield (number of atoms removed per ion impact) varies with porosity. For example, the yields in a CHF@sub 3@ discharge of a 78% porous Xerogel film and a thermal oxide film are 0.88 and 0.58, respectively. One possible explanation for this difference are residual organic groups present in the Xerogel films. We have also characterized the surface modifications after a partial etch by X- ray Photoelectron Spectroscopy (XPS). Finally, we compare the patterning of the Xerogel films to thermal oxides.

2:40pm **MS-TuA3 Surface Science of Tungsten CMP Removal***,* ***D.J. Stein****, D.L. Hetherington,* Sandia National Laboratories*; J.L. Cecchi,* University of New Mexico

Chemical mechanical polishing (CMP) is the predominant method for planarization and metal damascene processing during manufacture of submicron integrated circuits (IC). Tungsten CMP is used to remove excess tungsten after non-selective chemical vapor deposition in contacts and vias. We have investigated possible mechanisms of tungsten removal under typical IC manufacturing conditions. Previous models for tungsten CMP tungsten suggested that the dominant removal mechanism was the formation of a blanket oxide which was removed by mechanical abrasion.@footnote 1@ We used an electrochemical cell that allowed measurements of the tungsten oxidation rate and the removal rate. We found that the oxidation rate was between 0.01 and 0.1 of the tungsten removal rate, indicating that blanket oxidation does not play a significant role in tungsten removal.@footnote 2@ To elucidate the mechanisms responsible for tungsten removal, we undertook a number of additional investigations, including AFM and TEM imaging, correlations of the polish rate and process temperature dependence with the slurry constituent concentrations, and in-situ measurement of the friction and adhesion between the slurry colloid and the tungsten surface.@footnote 3,4@ We interpret our data with a heuristic model.@footnote 5@ It is shown that the empirical form of the heuristic model fits all of the data obtained. The mechanism also agrees with the limiting cases that were investigated. This mechanism captures the observed relationship between polish rate, pressure, velocity, and slurry chemistry. @FootnoteText@ @footnote 1@F. B. Kaufman et al., J. Electrochem. Soc. 138, 3460, 1991. @footnote 2@D. Stein et al., J. Electrochem. Soc. 145, 3190, 1998. @footnote 3@D. Stein et al., J. Electrochem. Soc. 146, 376, 1999. @footnote 4@D. Stein et al., submitted to J. Mater. Res. @footnote 5@D. Stein et al., accepted for publication in J. Electrochem. Soc.

3:00pm **MS-TuA4 Yield Improvement Through Multizone Uniformity Control of a CMP Process Utilizing a Pre and Post-Measurement Strategy***,* ***J. Moyne****, K. Khan,* University of Michigan*; J. Colt, J. Chapple-Sokol, R. Nadeau, P. Smith,* IBM*; T. Parikh,* SEMATECH **INVITED**

Achieving good uniformity process control in Chemical Mechanical Polishing (CMP) requires a representative uniformity metric and strong models relating this metric to process tunable inputs. Previous efforts in CMP uniformity control have yielded acceptable results utilizing a Center-to-Edge (CTE) first order non-uniformity metric. Closer analysis of post CMP process non-uniformity, however, reveals significant higher order non-uniformity components such as the center "dimple" and outer "doughnut" regions. These non-uniformity characteristics are due in large part to upstream CVD processing. Utilizing a multi-zone approach to uniformity modeling, a more accurate mathematical model of CMP uniformity has been identified. An optimization function has been developed based on minimizing the removal profile slopes as well as the absolute value of the area under the removal curve. The model and function have been utilized to customize a thickness and uniformity multivariate run-to-run software control solution for the process. The controller is based on the Generic Cell Controller structure, which is a proven enabler for run-to-run control for a number of processes including CMP, vapor phase epitaxy, and etch. The control algorithm is a zero'th order adjustable linear approximation two-stage algorithm with EWMA noise filtering. This algorithm, which supports first order linear and non-linear models, has been demonstrated to be effective in CMP CTE and thickness multivariate control. The control solution has been enhanced to utilize both pre and post CMP process metrology along with process models to suggest process recipe modifications on a run-to-run basis. Results indicate improved control of CMP process non-uniformity qualities of interest. Further, the results quantify the significant benefit of utilizing pre-metrology (feedforward) information in addition to traditional post metrology (feedback) in determining control recipe advices.

3:40pm **MS-TuA6 Modeling, A Tool for Technology Development***,* ***J.L. Garcia-Colevatti****,* Intel Corporation **INVITED**

Technology CAD, TCAD, is a term that describes a collection of model-based tools and methodologies that are used to assist process technology development, IC manufacturing control and the coupling of process specific behavior to products design. Different levels of model complexity, physics content and accuracy are needed depending on the development stage of a particular technology. The continuos need to understand and solve ever more difficult problems rapidly without escalating costs has forced us to draw and integrate results from multiple disciplines, enabling us to keep up with the relentless pace of silicon technology evolution. This presentation will review the scope of these tools, the infrastructure required for their rapid development and deployment and the benefits that result from their application to the exploration, development and manufacturing of new process technologies.

4:20pm **MS-TuA8 Simulations of TiN Barrier Films Deposited by I-PVD on High Aspect Ratio Features: Macrostructure and Composition***, M. Li,* ***S.K. Dew****, M.J. Brett,* University of Alberta, Canada*; T.J. Smy,* Carleton University, Canada

TiN films are extensively used as barrier layers for aluminum, tungsten, as well as copper in modern VLSI metallization processing. However, the properties of TiN are significantly dependent upon the microstructure and composition of the film. Physical vapor deposition is a technology commonly adopted for TiN barrier deposition, but recently the ionized variant, I-PVD, has attracted interest for deep sub-micron processes. In this work, by considering the adsorption and desorption of ionic and neutral nitrogen species, N and N2, and the reflection within the micro-features, the film growth simulator, GROFILMS, is used to study the film microstructure and composition over high aspect ratio topography in an I-PVD system. The effects of the film deposition conditions such as the total titanium flux, fraction of titanium ions, partial pressure of nitrogen, degree of nitrogen dissociation, substrate bias and film deposition temperature are investigated. In particular, the simulations demonstrate that ion impact energy and surface diffusion are two major processes determining the properties of TiN barrier films through control of the film density.

4:40pm **MS-TuA9 Investigation of Si and SiO@sub 2@ Etch Mechanisms Using an Integrated Surface Kinetics Model@footnote 1@***, **D. Zhang**, M.J. Kushner,* University of Illinois, Urbana

Computer aided development of new plasma etching processes requires a fully integrated plasma equipment and surface chemistry model to account for the interaction between bulk and surface processes. This is particularly important when different surfaces in the reactor (i.e., wafer, photoresist, walls, window) react differently with plasma generated species. To address these plasma-surface interactions throughout the etch chamber, and their influence on bulk plasma properties, the Surface Kinetics Model (SKM) was developed and integrated into the Hybrid Plasma Equipment Model (HPEM), a 2-D plasma plasma simulation tool. The SKM simulates the surface coverage and reactions of surface residence species using the flux of reactants from the HPEM. Ion energy and passivation layer thickness dependent processes are included. Patterned wafers can be addressed by partitioning the surface sites. The SKM was used to investigate the surface reaction mechanism for the fluorocarbon etching of SiO@sub 2@. The model includes formation of a passivation layer by CF@sub x@ radicals, its etching by F atoms and its sputtering by ions. The SiO@sub 2@ etch process is represented by 3 (or more) steps, which starts with formation of a CF@sub x@-SiO@sub 2@ complex which, with ion-energy activation, desorbs CO@sub x@ or COF@sub x@ products which diffuse back through the passivation. The remaining =SiF@sub x@ surface site is successively passivated by F atoms diffusing through the passivation, until ion activation desorbes the SiF@sub x@. Results will be discussed for C@sub 2@F@sub 6@ etching of SiO@sub 2@ in inductively coupled, rf biased reactors as a function of ICP and bias power, demonstrating the dependence of etch rates and selectivity on passivation layer thickness. @FootnoteText@ @footnote 1@This work was supported by SRC and LAM Research.

5:00pm **MS-TuA10 Design of a Dual Frequency PECVD Reactor for Advanced Integrated Circuits Processing***, **S. Raoux**, M. Mudholkar, W.N. Taylor, M.A. Fodor, J. Huang, D. Silvetti, K. Fairbairn,* Applied Materials

A capacitively-coupled PECVD reactor was designed using a high-temperature AlN ceramic heater with an embedded RF electrode. The first electrode (at the wafer) is biased at low frequency (350kHz) to control ion bombardment during film growth. The second RF electrode (or showerhead) is biased at 13.56MHz and has conical holes providing a (soft) hollow cathode effect for intense molecule dissociation and ionization efficiency. In this paper, we present advances in Si3N4 film deposition using a dual frequency RF plasma and SiH4, NH3 and N2 as precursor gases. We investigate the relation between ion energy and dual frequency plasma impedance, and correlate plasma potential with the film density and etch integrity. A SPICE (Simulation Program with Integrated Circuits Emphasis) model of the plasma reactor was determined. The model is compared to experimental data, and it is shown that the film stress is correlated to the phase angle (I/V) of the low frequency bias and to the heater electrode capacitance. We will present applications of this reactor for deposition of low-temperature (400C) Inter-Metal-Dielectric films and High Temperature processes (550C) for Pre-Metal-Dielectric films.

Manufacturing Science and Technology Group
Room 611 - Session MS-WeM

Metrology I

Moderator: B. Van Eck, Sematech

8:20am **MS-WeM1 Low Open Area Endpoint Detection of Plasma Etching Processes*, B.E. Goodlin, H.H. Sawin,*** Massachusetts Institute of Technology

Accurate determination of endpoint in plasma etching processes is essential to decrease defects due to both incomplete clearing of the etched material and excessive overetch of the underlying material, leading to a loss of dimension control. This is particularly challenging for low open area etches (<1%), where traditional sensors are at the limits of their sensitivities in determining endpoint. In previous work, we have investigated the use of multivariate analysis to improve the signal to noise of optical emission spectroscopy (OES) data. Improvements of signal to noise of well over 1000% was achieved versus the typical univariate endpoint detection mechanisms employed in industry. Nevertheless, in the lowest open area cases(<1%), difficulty was encountered due to the nonstationary time series behavior of the optical emission signals during main etch. This nonstationary behavior greatly obscured the ability to detect endpoint in these cases. In this work, we have explored several techniques by which to remove time series behavior in optical emission signals. After applying appropriate time series models, the revised data was then analyzed using a multivariate Hotelling's T2 method to see whether endpoint could adequately be detected in low open area etches. The results from historical data are very encouraging and further studies are underway to determine the robustness of this technique.

8:40am **MS-WeM2 Broad Band RF Based Sensing and Control of Reactive Ion Etching*, C. Garvin,*** *J.W. Grizzle,* The University of Michigan

This talk will present continued advances in the development of an in-situ RF sensing system for plasma assisted microelectronics processing. RF sensing has long been considered a potentially valuable diagnostic. However, despite much effort, results to date have been limited and mostly qualitative. Our past work has indicated that these limitations are due to inherently poor sensitivity in passive RF sensing. In addition, we have shown significantly better sensitivity to process conditions using a novel multi parameter variation of microwave spectroscopy, referred to as Broad Band RF. On a research reactor (GEC) and for simple chemistries, a non commercially viable version of the broad band probe was shown to be substantially better than standard RF sensing approaches at detecting process setpoints.@footnote 1@ Recently, we have developed a commercially viable non-contacting version of our broad band sensor, and have implemented it on a Lam 9400. The sensor has been used to develop an etch rate model for polysilicon in a Cl2/HBr chemistry.@footnote 2@ In this talk, we will present continued progress towards process control with the broad band sensor. Initial results indicate the broad band sensor is capable of endpointing performance that is at least as good as standard photo diode based OES methods. We will present further advances in a broad band etch rate model. Initial data indicates that an oxide etch rate model is at least as good as the polysilicon etch rate model already presented. Finally, we will investigate physically dominated and chemically dominated etch regimes in more detail. We will present results of initial work in these areas. @FootnoteText@ @footnote 1@ Garvin, C. Grimard, D. S., and Grizzle, J. W. "Advances in Broadband RF Sensing for Real-time Control of Plasma-Based Semiconductor Processing" JVSTA, Jul/Aug 1999 @footnote 2@ Garvin, C. Bilén, S. G. Stutzman, B. S. and Grizzle, J. W. "Implementing Broad Band RF Sensing on a Lam 9400 Reactor", The Electrochemical Society 195@super th@ Meeting, May 2-6 1999

9:00am **MS-WeM3 Diagnostic and Plasma Etch Endpoint Applications using Full Spectrum Optical Emission Spectroscopy*, H.M. Anderson,*** University of New Mexico*; S. Gunther, W. Branagh, J. Rivers, B. Fry,* CETAC Technologies

The advantages of full spectrum optical emission spectroscopy (OES) over monochromator based systems has been readily demonstrated. Traditionally, monochromator based systems have been used to determine endpoint by monitoring one or two strongly emitting wavelengths. For exposed open areas of <1.0%, a more sensitive approach is required for the next generation of chips. Array detector based systems can provide a wealth of spectral information from a variety of potentially useful gas phase emitting species. In the case of particularly challenging applications such as reverse mask shallow trench isolation (STI) and contact etches, utilization of the full optical emission spectrum has been shown to provide tangible benefits. Production facility results regarding these and other demanding applications will be presented. The talk will largely focus on oxide etching in AMAT MXP and AMAT HDP platforms. Evolving Window Factor Analysis (EWFA) and Multiple Curve Resolution (MCR) are the princpal multivariate techniques used in the analysis. They allow one to dynamically track the principal components of the oxide etch process. EWFA is also shown to useful for automatic fault detection. MCR is used to depict the dynamic rate of formation (or depletion) of the principal chemical species in the plasma during the etch.

9:20am **MS-WeM4 Real Time Control of Plasma Deposited Optical Filters by Multiwavelength Ellipsometry*, T. Heitz,*** CNRS-Ecole Polytechnique France, FRANCE*; P. Bulkin,* CNRS-Ecole Polytechnique France*; A. Hofrichter,* CNRS-Ecole Polytechnique France, FRANCE*; F. Chataignere, B. Drevillon,* CNRS-Ecole Polytechnique France

Multilayer and gradient coatings allow the integration of advanced functionnalities. But due to their complexity, in-situ probes are necessary to control the process and obtain a good reproducibility. Our optical filters (Fabry-Perot, anti-reflective or heat-reflecting coatings) consist of SiO@sub x@N@sub y@ multilayers and/or graded index profile structures deposited at room temperature in an IDECR reactor on glass, PMMA or polycarbonate. Due to its thickness sensitivity, multiwavelength UV-visible phase-modulated ellipsometry was chosen to monitor the growth process. The control strategy is based on minimising the sum of the distances between the measured point and the theoretical end point of the optical trajectory at 4 wavelengths. This strategy is proved to be very efficient and independent of the deposition rate. As substrates are thick and transparent, the theoretical trajectories have been calculated using the incoherent reflection model which takes into account backreflection. Moreover, to model possible anisotropy effects, optical calculations have been developed based on a non-diagonal dielectric matrix for the susbtrate. In order to build a closed-loop automation system, efficient algorithms have been developed to determine in real time the optical properties and the current deposition rate. Using 4-wavelength optical data, 1 sec step acquisition and appropriated dispersion laws, the refractive index and the current thickness can be calculated which allows to correct in real time the gas flow values. The high quality of the filters deposited using the ellipsometric monitoring system is demonstrated by comparing experimental and theoretical transmission/reflection curves in terms of peak positions and bandwidth.

9:40am **MS-WeM5 Real Time and Run-to-Run Process Control of Plasma Processes Using Internal Machine and External Sensor Data*, F.H. Bell,*** *D. Knobloch,* Infineon Technologies AG, Germany*; J. Zimpel, K. Voigtlaender,* Fraunhofer Institute, Germany*; J. Mathuni, P. Hoehmann,* Infineon Technologies AG, Germany

An automatic extraction of key numbers (per wafer) from internal raw machine data and external sensor data has been established for the supervision of plasma equipment and processes in high volume logic and DRAM fabs. The integration of external in-situ sensors in the fab-network of the different sites is realized using the home-built equipment integration software TICS (Tool Integration Concepts and Systems). One main goal of the external sensor integration is to establish plug-and-play modules, i.e. rapid integration of suitable sensors tackling equipment and process faults. Furthermore, analyses of online data over long time periods give information on tool- and chamber- matching, long term stability, trends over cleaning cycles, influence of recipe / product mix, first wafer / conditioning effects and arcing phenomena. Currently in use are electrical and optical sensors, such as optical emission spectroscopy, interferometry, ion flux probe, plasma impedance monitor. etc.. However, the more useful data is collected the more attention has to be paid on intelligent data treatment. A typical example is the need of data reduction in order to extract only process and equipment relevant key numbers. It will be shown that algorithms, such as principal component analyses, are excellent candidates to simplify the use of process control methods in a manufacturing environment. This talk will analyze the different approaches to control equipment and processes and the challenges that are faced by the semiconductor industry as the automation becomes more and more mandatory in the competition of IC-fabrication. Examples of real time control will also be given to demonstrate the benefit of sensors on manufacturing issues.

10:00am **MS-WeM6 Advanced Endpoint Capability in Plasma Processing Equipment Using Interferometer Technique*, T. Ni,*** Lam Research Corp.

A new interferometer system has been developed at Lam Research Corp.. It provides capability of in-situ etch depth measurement and can be used as an endpoint device when the traditional OES system fails. It consists of a light source and a CCD array spectrometer. A fiber optic cable delivers the light from the lamp to the center of a wafer being processed at normal incident angle. The CCD array spectrometer records the spectrum of the reflected light from the wafer surface. The optical window for light access is engineered to prevent polymer deposition. The analysis of the spectrum yields the thickness information of the films on the wafer. Frequently, the etch depth can be obtained by simply counting the interferometric fringes. With the use of a deep UV light source, an etch depth as shallow as 1000A can be accurately measured. The advantage of the interferometer is demonstrated for applications such as shallow trench isolation (STI) and recess etch. The traditional OES system cannot provide an endpoint signal since there is no stopping layer. Using the interferometer, the etch depth is monitored and etching process can be stopped when the desired depth is reached. In the case of poly gate etch with a very thin (10A-20A) gate oxide underlayer, the interferometer can be used to predict the remaining poly layer thickness so the process can be changed from the main etch process to the overetch process before the oxide layer is exposed. A typical overetch process has greater than 200:1 selectivity to underlayer, while the main etch selectivity typically is much less. Thus, punching-through of the oxide layer is prevented. The details of the interferometer and process results will be presented and discussed.

11:20am **MS-WeM10 Reaction Sensing in Multicomponent CVD Processes using an Acoustic Sensor*, L. Henn-Lecordier*,** *G.W. Rubloff, J.N. Kidder, Jr.,* University of Maryland*; C. Gogol, A. Wajid,* Leybold Inficon Inc.

Downstream or in-reactor chemical sensing provides information about the extent of reaction in a chemical vapor deposition process. Prior approaches have employed mass spectrometry or optical techniques. Here we utilize for this purpose an acoustic sensor which measures the sound velocity in bicomponent or multicomponent gas mixtures in the viscous flow regime. This sensor, the recently introduced Leybold Inficon Composer@super TM@, has been employed primarily to measure and confirm bicomponent inlet mixtures from MOCVD bubbler sources for process reproducibility. Here we have explored its use in downstream locations, either after or at the reactor, where the influence of the CVD reaction can be monitored in the form of gas composition changes resulting from reactant depletion and/or product generation. For W CVD processes, the heavy WF@sub 6@ reactant mixed with H@sub 2@ or SiH@sub 4@ provides substantial molecular weight contrast, so that depletion of WF@sub 6@ is readily observed. To achieve sufficiently high pressures (~50-100 torr) for acoustic wave propagation in a viscous medium, sensing is carried out downstream of a mechanical pump. For H@sub 2@/WF@sub 6@ mixtures, depletion levels as small as 1% or less are detectable. This is sufficient for wafer state thickness metrology and monitoring of reactant utilization efficiency, suggesting a promising approach to reaction metrology. However, the corrosive nature of the reactant gasees normally necessitates a N@sub 2@ purge of the pump. With the molecular weight of typical H@sub 2@/WF@sub 6@ mixtures close to that of N@sub 2@, this degrades sensitivity to of order several %. A variety of other implementation issues will be discussed, along with an assessment of a variety of process applications.

11:40am **MS-WeM11 Improvements in Wafer Temperature Measurements*, A. Cardoso*,** *A.K. Srivastava,* Eaton SEO

Accurate and repeatable wafer temperature measurement and control is critical in many semiconductor processing applications. Many of these applications are done at moderate pressures (.5 - 2 Torr) where thermal contact resistance between the wafer and a contact temperature probe is high, and could vary wafer-to-wafer. The result is an unpredictable difference between the actual wafer temperature and contact measurement probe due to heat transfer across this interface from exothermic reactions, hot plasma gases, or radiant heating. In some applications, this temperature difference is so great that backside helium cooled electrostatic chucks are used to minimize this effect. In many applications, the use of this type of solution is not practical but accurate and repeatable wafer temperature measurement is still required. A new temperature sensor has been developed that utilizes gas injection through a pinhole in a thermocouple pad that creates a "micro-environment" between the pad and the wafer. This results in reduced thermal contact resistance, and more accurate and repeatable temperature measurement. Temperature data on the operation of this sensor during wafer processing will be presented, showing significant improvement over prior state of the art. Data verifying the robustness of this probe will be shown. Additionally, diffuse reflectance spectroscopy will be used as a non-contact temperature measurement technique to corroborate data from the new gas-cushion thermocouple.

Manufacturing Science and Technology Group
Room 611 - Session MS-WeA

Metrology II

Moderator: A.C. Diebold, Sematech

2:00pm **MS-WeA1 Micrometrology with Scanning Probes***, **H.K. Wickramasinghe,*** IBM T.J. Watson Research Center **INVITED**

Scanning Probe Microscopes (SPM) have become valuable instruments for development and quality control in the semiconductor industry. They provide new capabilities for inspection and metrology of surfaces on a sub-micron scale. The key to their operation is the positioning and scanning of a small tip, or probe, at a minute distance over the surface. The ability to track the position of a surface with an accuracy of the order of a nanometer is advancing the frontiers of micro- or nano-metrology in the semiconductor industry. The standard Atomic Force Microscopes (AFM), using a conical shaped tip, is the most widely used type of SPM for inspection and metrology. This technology essentially measures depth of structures with high precision. Recent technical developments have added the capability to accurately measure width of lines and trenches, using a flared tip and an improved scanning and tracking method for the tip. Other techniques have evolved that measure magnetic properties on the nanometer scale. The talk will review the recent developments of scanning probes with special focus on applications to manufacturing.

2:40pm **MS-WeA3 Chemical Process Sensing using Mass Spectrometry in Multicomponent Reaction Systems***, **Y. Xu,** T. Gougousi, N. Gupta, J.N. Kidder, Jr., G.W. Rubloff,* University of Maryland

A significant number of CVD applications in VLSI manufacturing, such as CVD of W, TiN, SiO@sub 2@, Cu, and more complex high K materials, involve multicomponent reactant mixtures. We have investigated experimentally W CVD processes from H@sub 2@/WF@sub 6@ mixtures in attempts to develop mass spectrometry based thickness and rate metrology approaches. This direction poses a variety of challenges, both fundamental and practical. First, the choice of reactant stoichiometry is dictated by the mechanistics of the application, and typically an overabundance of one reactant is required, so that transport of the other is at least in part rate-limiting. This determines which species is suitable for measurement of reactant depletion for deposition metrology. For example, in SiO@sub 2@ CVD from SiH@sub 4@/N@sub 2@O, the N@sub 2@O must be in large excess to assure fully oxidized, high quality material, while in W CVD, low H@sub 2@ to WF@sub 6@ ratio (usually 4) is required to achieve good conformality in via filling. Second, gaseous species may undergo substantial wall reactions, which in turn depend on previous process history (e.g., in W CVD, HF and WF@sub 6@ condense on walls and subsequently desorb slowly). Third, the mass spectrometer ionizer provides a second reaction region (in addition to the wafer), contributing to the depletion of the reactants and occasionally generating the same products as the CVD reaction itself (HF in W CVD from H@sub 2@/WF@sub 6@ precursors). Fourth, the combination of wall adsorption/desorption and sensor reactions can lead to another extraneous source of products. In the H@sub 2@/WF@sub 6@ system sustained H@sub 2@ flow after the WF@sub 6@ flow is terminated leads to sensor generated HF utilizing the WF@sub 6@ desorbing from the walls. We illustrate these phenomena through both experimental and modeling results, and we assess key aspects of the general approach for multicomponent CVD systems.

3:40pm **MS-WeA6 Mechanisms for the Production of Atomically Flat Surfaces Studied by Scanning Probe Microscopy@footnote 1@***, **S.C. Langford,** R.F. Hariadi, J.T. Dickinson,* Washington State University

Chemical-mechanical polishing (CMP) is a critical step in the fabrication of integrated circuits, yet the complex interactions between chemical and mechanical effects in CMP are still not well understood. We examine layer by layer material removal and deposition under conditions of combined mechanical stress and chemistry using scanning probe microscopy (SPM), where the SPM tip serves as a model single asperity/abrasion particle. We focus on monolayer-deep etch pits on a model, biomaterial substrate, single crystal brushite (CaHPO@sub 4@@super .@2H@sub 2@O). Scanning across monolayer steps in undersaturated solutions at high contact forces produces distinct wear tracks due to localized double kink nucleation. Low contact force scanning in supersaturated solution produces localized deposition along steps in the scanned region. The latter suggests a novel method of producing atomically flat surfaces by mechanically controlled re-crystallization. These results allow quantitative models of wear and deposition to be developed and tested. @FootnoteText@ @footnote 1@This work supported in part by the NSF Surface Engineering and Tribology Program under Grant CMS-98-00230.

4:00pm **MS-WeA7 Investigation of Thermal Curing of an Organic Low-k Spin-on Dielectric by Variable-Angle Spectroscopic Ellipsometry***, **F. Yang,** W.A. McGahan,* Nanometrics, Inc.*; C.E. Mohler, L.M. Booms,* The Dow Chemical Company

As device features of ultra-large-scale-integrated (ULSI) circuits continue to shrink, a new type of dielectric material with a low dielectric constant k is needed for replacement of SiO2 as the insulating material between multi-level interconnects. Dow Chemical's SiLK* semiconductor dielectric@footnote 1@ has been investigated as a potential candidate for the low-k dielectric. SiLK dielectric thin films are formed by spin-on process, followed by a thermal curing process, which determines the mechanical, electrical, and chemical properties. A properly cured SiLK dielectric thin film offers a dielectric constant of 2.65, along with merits of high thermal stability, excellent gap-fill properties, high solvent resistance, and low moisture absorption. In this paper, optical properties of SiLK dielectric thin films cured at different conditions are characterized using variable-angle-spectroscopic ellipsometry. Correlation is found between the optical constants in the ultra-violet wavelength region, and the extent of the cure (cure time and cure temperature). Based on the relationship between optical constants of SiLK dielectric and its curing condition, a single-parameter empirical interpolation model is developed to describe the dispersion of SiLK dielectric's optical constants. Despite a single adjustable parameter, this interpolation model closely tracks the variation of SiLK dielectric's optical constants at different curing conditions. With this model, in-line monitoring the cure of SiLK dielectric thin films can be realized. @FootnoteText@ @footnote 1@ SiLK* is a trademark of The Dow Chemical Company.

4:20pm **MS-WeA8 Assessment of Quadrupole Mass Spectrometry as an In Situ HDP-CVD Process Diagnostic Technique***, **J.A.B. Van Hoeymissen,*** IMEC, Belgium*; C. Hughes,* BOC Edwards industrial resident at IMEC, Belgium*; M. Heyns,* IMEC, Belgium

Process control using in situ techniques is an attractive aid to semiconductor manufacturing. The potential of quadrupole mass spectrometry (QMS) has been assessed as an in situ sensing technique for a silicon oxide high density plasma chemical vapour deposition (HDP-CVD) process. In this paper it is shown that in situ measurements using mass spectrometry can play an important role in the areas of process monitoring, process control and process recipe optimization. The species present in the chamber were analysed via a gas sampling system, with pressure reducing orifice, installed just below the deposition chamber to ensure a representative, real-time, sensitive measurement. Correlation between in situ observations and oxide layer thickness was investigated. H@sub 2@O is an important reaction by-product of the deposition reaction. A direct and highly sensitive correlation between the H@sub 2@O+ signal and oxide layer thickness could be observed. In fact, this QMS signal could be used to monitor oxide layer thickness during deposition. In addition, the [H@sub 2@O+] was found to increase exponentially during deposition. During consecutive depositions of P-doped oxide (PSG) layers, the thickness of the first layer was systematically about 2% higher than the subsequent layers. In situ analysis was carried out monitoring the time resolved intensity of mass 34 (PH@sub 3@+) during the first three PSG depositions. This intensity was clearly higher during the initial phase of the first PSG deposition. The composition of the layers were analysed with SIMS. The results indicate the phosphorus content of the first layer is significantly higher during the initial phase of the deposition. These combined results indicate a higher initial [PH@sub 3@] in the deposition chamber during the deposition of the first PSG layer. These observations prompted an adaptation of the chamber conditioning and clean recipe preceding the first PSG deposition, resulting in the disappearance of the first wafer effect.

4:40pm **MS-WeA9 Determining Ion Flux and Ion Energy from Radio-Frequency Current and Voltage Measurements***, **M.A. Sobolewski,*** National Institute of Standards and Technology

To obtain optimal results from plasma processing, the flux and energy of ions incident on the substrate must be carefully monitored and controlled. Several diagnostic techniques are used to measure ion flux and ion energy, but these techniques are typically not very compatible with the processes and reactors used by industry. Methods have been proposed for determining ion properties from the applied current and voltage waveforms, which can be measured in commercial reactors. However, such methods are usually not very accurate because they rely on false or untested assumptions. Here, a new, more accurate method is presented which makes use of a complete model of the time-dependent ion dynamics in the plasma sheath. The model was validated by comparison to independent measurements of ion flux, ion energy, and time-resolved optical emission, for high-density discharges in an inductive GEC Reference Cell. Measurements were performed for discharges in Ar, Ar/SF@sub 6@, and Ar/Cl@sub 2@, for inductive source powers up to 370 W, rf bias powers up to 100 W, rf bias frequencies of 0.1-13.56 MHz, and pressures of 0.67-4.0 Pa. An analysis of the sensitivity of ion flux and ion energy results to model parameters will be presented, along with comparisons showing the improvement in accuracy obtained by the new technique.

5:00pm **MS-WeA10 Linking Process and Structure using Automated Analysis of AFM Images*, D.A. Chernoff*,** *D.L. Burkhead, C.S. Cook,* Advanced Surface Microscopy, Inc.

By volume of product, the optical disc industry is the largest nanotechnology activity today. On DVDs (Digital Versatile Discs), the smallest features are about 400 nm long, 320 nm wide, 120 nm high, with a track pitch of 740 nm. Consumers need optical discs whose electrical performance during playback is consistently within specifications. Existing disc analyzers report electrical test results and engineers respond to deviations by adjusting process variables. This method provides only indirect control because the process variables determine the microstructure of the master, stamper and replica and it is that microstructure which determines ultimate electrical performance. A method is needed to examine microstructure so that one can see how each process variable affects various aspects of microstructure and to see how each aspect of microstructure affects performance. Automated, high accuracy analysis of Atomic Force Microscope (AFM) images provides the missing link. We measured the following parameters: track pitch, bump height, bump width and length (at various threshold levels), bump length, and four sidewall slope angles, in each case reporting mean, standard deviation and other statistics. From each 10 um image of a DVD stamper, containing about 100 bumps, we tabulated about 1000 values. Bump width increased with bump length, correlating with a corresponding increase in amplitude with pulse duration when a finished disc is played. Where sidewall angle deviated from the norm, we reviewed the image data to identify the specific nature of the defect. The results were statistically robust not only for mean values, but also for standard deviations, so that we could compare process variation from different pieces of equipment. Thus, feature geometry will no longer be a hidden variable in the path between controlling production equipment and observing the good or bad electrical performance of a finished disc.

Topical Conference on Emerging Opportunities and Issues in Nanotubes and Nanoelectronics
Room 6C - Session NT+NS+EM+MS-WeA

Nanotubes: Growth, Characterization and Properties I
Moderator: S.B. Sinnott, University of Kentucky

2:00pm **NT+NS+EM+MS-WeA1 Making and Modifying Carbon Nanotubes*, R.E. Smalley*,** Rice University **INVITED**

The last year has produced exciting developments in our ability to produce and modify single wall carbon nanotubes (SWNT). New experiments have shown the feasibility of producing nanotubes in an efficient gas-phase process, sometimes having diameters down to approximately 0.6 nm. These methods involve chemical vapor deposition in high-pressure carbon monoxide. We are now pursuing this growth technique as a potentially viable means for cost-effective production of large amounts of SWNT. Development of new methods for purification and characterization of nanotubes has given new insight into their growth mechanisms. I will present new data on the morphology and length distributions of SWNT grown by traditional laser-oven methods, and outline new results on the behavior and characteristics of tube samples. Perhaps the most remarkable developments have been in the chemistry of SWNT as a new molecular species. Several groups have discovered means of covalent attachment of other chemical species to the tube ends and sidewalls. This derivatization significantly modifies the properties of SWNTs, permits the first true solutions of tube segments, and opens the door to a remarkable new realm of chemistry, materials science, and electronics.

2:40pm **NT+NS+EM+MS-WeA3 Roles of Fe, Co, and Ni in the Formation of Single-Walled Carbon Nanotubes and Encapsulated Nanoparticles*, J. Jiao,*** Portland State University

The preparation and structural properties of carbon nanoclusters synthesized by having the transition metals Fe, Co, and Ni react with carbon in three different methods were investigated comparatively with the focus on single-walled nanotubes and encapsulated nanoparticles. The carbon nanoclusters were synthesized first by the high temperature (~3000°C) and high carbon-content process of the conventional arc discharge, secondly by the high temperature but low carbon-content process of the modified arc-discharge, and finally by the relatively low temperature (~500°C) process of catalytic decomposition of carbon monoxide (CO). The samples were characterized with respect to morphology, internal structure, and related properties. The carbon nanoclusters prepared by three different methods appear quite different on the surface, but have features in common that this report emphasizes. The same element can apparently serve different functions, serving as catalyst under one set of condition, and being encapsulated into the growing cages in a different environment. The elements of the iron group (Fe, Co, and Ni) were known as catalysts for growing the single-walled nanotubes and strings of spherical particles in conventional arc discharge, but could be encapsulated into the graphitic particles in the modified arc discharge and the CO disproportion that this study demonstrates. It was found that variation of the metal-to-carbon ratio is required to make these elements assume the double roles of either catalyst or encapsulant. In this report, an assembly of growth phenomena of carbon nanoclusters indicating the roles of the Fe, Co, and Ni will be presented. The growth mechanisms of these structural phenomena in relation to the preparation conditions in particular to the ratio of carbon content in the reaction chamber during the preparation are discussed.

3:00pm **NT+NS+EM+MS-WeA4 Plume Diagnostics During Carbon Nanotube Production by Laser Ablation*, S. Arepalli,*** G. B. Tech./Lockheed Martin*; C.D. Scott,* NASA/Johnson Space Center

We report recent results of our plume diagnostics during carbon nanotube production by double pulse laser oven method. The evolution characteristics of different species in the plume from different regions of the laser ablated plume will be presented. Transient emission data is compared with plume images to formulate dynamics of plume expansion. Vibrational and rotational temperatures of C@sub 2@ and C@sub 3@ are estimated by comparison with computations. Excitation spectra of LIF are used to deduce ground state temperatures and populations.

3:20pm **NT+NS+EM+MS-WeA5 Synthesis and Integration of Carbon Nanotubes*, H. Dai,*** Stanford University **INVITED**

This talk focuses on controlled growth and properties of multi-walled and single-walled carbon nanotubes on catalytically patterned substrates. It will be shown that new possibilities are opened up in nanotube science and applications by synthesizing nanotubes at desired locations and orientations in ordered fashions. A recently developed chemical vapor deposition method for high quality single-walled nanotubes is combined with microfabrication methods to reliably integrate single-walled nanotubes into various electrical architectures. The transport properties of individual single-walled nanotubes will be presented. Functional nanotube electrical devices with advanced performances will be shown. Issues in further control of nanotube growth will be addressed.

4:00pm **NT+NS+EM+MS-WeA7 Growth of Vertically Aligned Carbon Nanotubes on Transition-metal Catalyzed Plain Silicon Substrates using Thermal Chemical Vapor Deposition*, Y.H. Lee,*** *Y.C. Choi,* Jeonbuk National University, Korea*; C.J. Lee,* Kunsan National University, Korea*; Y.B. Han,* Jeonbuk National University, Korea

Vertically aligned carbon nanotubes have been grown on a large area of transition-metal coated plain silicon substrates by thermal chemical vapor deposition method. We find that vertically aligned growth is critically dependent on the domain density in the transition metal cluster. Steric hindrance between nanotubes at an initial stage of the growth forces nanotubes to align vertically. Nanotubes are then further grown by the catalyst-cap growth mechanism. We also show emission patterns from aligned nanotubes. Our current approach of simple integration of stable field-emission displays on a large area puts a step forward to future display applications.

4:20pm **NT+NS+EM+MS-WeA8 Carbon Nanotube Tips: Structures and Properties***, **J. Han**, L. Yang, R.L. Jaffe,* NASA

A variety of structures and properties of carbon nanotube tips present challenges in understanding of electron tunneling and field emission of carbon nanotube materials. Topologically, a nanotube tip can be formed by joining a tube bulk and a cone or a half the fullerene. Different configurations can be resulted from arrangement of topological defects. Energetically favorable configurations are identified and classified using functional theory and molecular mechanics calculations. They are further used for electronic structure calculations based on tight-binding approaches. The location and intensity of localizes states at tips are studied as functions of the size and configurations of tips. The differences in localized stated between one and four-orbital calculations are also compared. Experimental results of carbon nanotube field emission properties are related to the calculations of the localized stated of nanotube tips.

4:40pm **NT+NS+EM+MS-WeA9 Electrochemical Deposition of Carbon Nanofilaments***, E. Anoshkina, **D. Zhou**, L. Chow, V. Desai,* University of Central Florida

Carbon nanofilaments are conventionally made from thermal catalytic chemical vapor deposition with carbonaceous gases as growth precursors. Based on their unique mechanical, thermal, and electrical properties, many applications of carbon nanofilaments have been realized in advanced technologies. We report here on a new method to prepare carbon nanofilaments, in which the nanofilaments have been made from organic solvents such as methanol through an electrochemical deposition process. Silicon wafers coated with Fe or Ni nanoparticles were employed as the electrodes, and the depositions were carried out at room temperature. It has been found that electrical field between the electrodes, conductivity of the solvent, and size of the catalysts play important roles in control of morphologies of the carbonaceous deposits. Furthermore, based on characterization of the nanofilaments using scanning electron microscopy, transmission electron microscopy, and energy dispersive x-ray spectroscopy, the formation and growth mechanism of carbon nanofilaments from the electrochemical deposition has been discussed.

5:00pm **NT+NS+EM+MS-WeA10 A Study on the Growth of Carbon Nanotubes with Respect to Process Conditions***, J.N. Srivastava, K.K. Awasthi, **C.D. Dwivedi**, G.N. Mathur,* Defence Materials & Stores Research & Development Establishment, India

Carbon nanotubes have been produced by graphite evaporation method in macroscopic quantities with reproducible results at different conditions. A study on the growth of CNT against the variation in Helium / Argon / Nitrogen pressure has been done and some interesting results are found with respect to geometry, density and alignment of the tubes. Total yield of the material is also found to be having correlation with the pressure and current. Material produced in different conditions has been characterized by XRD, SEM, TEM, TGA and FTIR techniques.

Manufacturing Science and Technology Group
Room 4C - Session MS-WeP

Poster Session

MS-WeP1 Effects of Trapped Charges on Hg-Schottky Capacitance-Voltage Measurement of N-type Epitaxial Silicon Wafers, *Q. Wang, **D. Liu**, J.T. Virgo,* Mitsubishi Silicon America Corp.

The accurate carrier concentration profiling is very critical during silicon wafer process such as dopant profiling measurements of epitaxial layer or ion implanation etc. The mercury probe (Hg-Schottky capacitance-voltage (CV)) is a standard method in this application. This method is however, very sensitive to the silicon wafer surface condition and is a challenging issue in semiconductor industry. A poor Schottky contact will produce an erroneous and misleading result. It was believed that the surface chemical preparation was an essential step to have a relatively accurate CV reading. Our recent study, however, showed that the surface chemical preparation is not the only factor. The electrical charges on surface are equally important to the CV measurement. This work studied this effect on the Schottky CV measurements in detail. A new method has been developed in which an electrical surface preparation has been used prior to the CV measurement. The new method significantly improved the accuracy and repeatability of CV measurement.

MS-WeP2 A Two-Dimensional Modeling Study of Pattern Dependent Etching@footnote 1@, ***B. Lay**, M.J. Kushner,* University of Illinois, Urbana

Pattern dependent etching has become an increasingly important problem as feature sizes have decreased. It has been observed that a large exposed region on a die in close proximity to fine features tend to decrease the etch rates of the small features. In order to have process-independent uniform etching, the cause of this phenomenon must be determined. Previous studies have shown that gas phase processes alone, particularly at low pressures (< 10-20 mTorr), are unable to explain these observations. In this paper, the results of a numerical study of pattern dependent etching will be presented. A 2-dimensional computer model has been developed which addresses current flow through both the solid wafer material and the plasma. The Plasma-Solid-Simulator (PSS) solves Poisson's equation coupled with the continuity equations for electrons and ions in the plasma, and current density in the bulk, on a triangular mesh. The equations are linearized and implicitly integrated using Newton's method. The PSS calculates the conduction and displacement currents flowing through a partially exposed wafer during the etching process and relates them to etching characteristics. Parametric results from the PSS will be discussed as a function of plasma power and pattern layout. The observed increase in electric fields surrounding the unmasked portions of the wafer may lead to additional electron heating. @FootnoteText@ @footnote 1@This work was supported by SRC, AFOSR/DARPA, Applied Materials and LAM Research

MS-WeP3 Plasma Etch-Back Coupled to Chemical Mechanical Polishing for Sub 0.18 µm Shallow Trench Isolation Technology, ***A. Schiltz**,* France Telecom, CNET-CNS, France*; L. Palatini,* ESPEO - Orleans University, France*; M. Paoli, M. Rivoire, A. Prola,* France Telecom, CNET-CNS, FRANCE

This paper presents a new etch-back planarization technique with counter-masking to pre-planarize Shallow Trench Isolation substrates before Chemical Mechanical Polishing (CMP). A pre-planarization step is necessary since CMP alone cannot provide effective planarization for sub 0.18 technology due to dishing effect . The pre-planarization step uses the principle of Two Layer Planarization (TLP)@footnote 1@ technique which consists in spin-coating a first photoresist layer, using a counter-mask for the lithographic step, flowing and curing the resist blocks in STI topographies, spin-coating a second photoresist layer to planarize the residual topography and transferring the final flat surface into the substrate using plasma etch-back. In difference with previous techniques, we used a special mask with oversizing and exclusion of all STI critical dimensions smaller than 1.55 µm, the zones with the smaller STI dimensions being masked using a special narrow lines grid. Such a masking strategy avoids any misalignment problem, the resized first photoresist blocks are reflowed in STI topographies, leading to an easy planarization by the second resist layer. Additionally, the lithographic step is a non-critical step using conventional i-line resist. The final surface is transferred into the oxide substrate using (Ar/CF4/ O2) gas mixture in a LAM 4520 plasma etching equipment. To allow simultaneous etching of resist and oxide, various gas mixtures of Ar/x/O2 or Ar/x/y/O2 were tested, with x and y being chosen among following fluorine gas : CF4 - SF6 - C4F8 - CHF3. The (Ar/CF4/O2) gas mixture was observed to fulfill the etch back requirements with better performance. Equality of etch rate in resist and in oxide can be adjusted by the O2/CF4 gas ratio. A design of experiment (DOE) was used to determine the optimum conditions of plasma transfer of the planarized profile into the substrate. No ARDE (aspect ratio dependent etching) was observed, but loading effect was observed. Equality of etch rate in resist and in oxide during profile etch back transfer depends on oxide/resist surface ratio and therefore on the STI mask density. Then, equality of etch rate can be adjusted by the O2/CF4 gas ratio. Finally, the pre-planarized wafer is polished by CMP, resulting in an effectively planarized topography with residual topography smaller than 50 nm. The technique is a non-critical lithographic technique scaleable for technologies below 0.18 µm. @FootnoteText@ @footnote 1@ A. Schiltz and M. Pons, J. of the Electrochem. Soc., Vol. 133, 1, 178 (1986)

MS-WeP4 Composition of Si/Ge Films in Structures, ***S. Soukane**, T.S. Cale,* Rensselaer Polytechnic Institute*; C. Werner, A. Kersch,* Siemens, Germany*; M. Bloomfield,* Rensselaer Polytechnic Institute

In order to achieve optimum performance in SiGe base bipolar technology, the film composition must be carefully controlled.@footnote 1@ A detailed surface reaction mechanism for the chemical vapor deposition of SiGe on Si(100), using mixtures of hydrogen, dichlorosilane, hydrogen chloride and germane (H2, SiH2Cl2, HCl, GeH4) is discussed in this paper. The kinetic model involves a set of twelve reactions with several intermediate surface species, and includes both deposition and etching.@footnote 2@ Two reactions describe the migration of adsorbed chlorine and adsorbed hydrogen between silicon and germanium sites. Deposition simulations over device topographies are used to test the proposed kinetic model. Deposited film profiles, concentrations of each surface species, and composition (Si/Ge ratio) as a function of position in the simulated films, are predicted using the proposed chemical model in EVOLVE.@footnote 3@ We compare simulation results with available experimental data. @FootnoteText@ @footnote 1@1SiGeBase Bipolar Technology with 74 GHz fmax and 11 ps Gate Delay, T. F. Meister, H. Schafer, M. Franosch, W. Molzer, K. Aufinger, U. Scheler, C. Walz, M. Stolz , S. Boguth, and J. Bock, IEDM 95, IEEE, p.95-739 @footnote 2@2Kinetic Modeling of SiGe Deposition with SiH2Cl2 and GeH4, M. Hierlemann, C. Werner and H. Schafer, Abstract No. 726 in Electrochem. Soc. Abstracts Vol. 96-1, 1996, p. 900. @footnote 3@3EVOLVE is a low pressure transport and reaction simulator. EVOLVE 5.0b was released in November, 1998 (copyright T. S. Cale, 1989-1998).

MS-WeP5 Development of New Etching Algorithm for Ultra Large Scale Integrated Circuit and Application of ICP(Inductive Coupled Plasma) Etcher, ***Y.-C. Lee**, K.-R. Byun, S.-H. Park, J.-W. Kang, E.-S. Kang, O.-K. Kwon, H.-J. Hwang, T.-W. Kim,* Chung-Ang University, Korea

We proposed proper etching algorithm for ultra-large scale integrated circuit device and simulated etching process using the proposed algorithm in the case of inductive coupled plasma (ICP) source. Proposed algorithm calculates interactions both in plasma source region and in target material region, and uses binary collision approximation (BCA) method when ion impact on target material surface. Proposed algorithm considers the interaction between source ions in sheath region (from Quartz region to substrate region). After the collision between target and ion, reflected ion collides next projectile ion or sputtered atoms. In ICP etching, because the main mechanism is sputtering, both SiO2 and Si can be etched. Therefore, to obtain etching profiles, mask thickness and mask composition must be considered. Since we consider both SiO2 etching and Si etching, it is possible to predict the thickness of SiO2 for etching of ULSI. In this work, selectivity of Si and SiO2 is more than 50. The distribution of ions is calculated by Monte Carlo method and analytic model (plasma density 1012/cm3, pressures 1âˆ¼20mTorr), and the energy (ion flux corresponding to Maxwellian velocity distribution) increases by potential difference in sheath region. Projectile ion moves in time step, has direction and energy. When ion collides targets or ions, direction and energy is changed by impact parameter from binary collision approximation method. Proposed algorithm is efficient for computer calculation and easy to apply other cases. Results of etching simulation using proposed algorithm agree to results of SEM. In conclusion, in the case of ICP type reactor, proposed algorithm is appropriated to obtain etching profiles for ULSI process.

Topical Conference on Emerging Opportunities and Issues in Nanotubes and Nanoelectronics
Room 4C - Session NT+NS+EM+MS-WeP

Poster Session

NT+NS+EM+MS-WeP1 Growth of Carbon Nanotubes at Low Temperature by Microwave Plasma-enhanced Chemical Vapor Deposition*, **Y.C. Choi**, D.J. Bae, Y.H. Lee, B.S. Lee,* Jeonbuk National University, Korea

We have grown carbon nanotubes at temperatures below 520 C by microwave plasma-enhanced chemical vapor deposition using methane and hydrogen gases. Carbon nanotubes were uniformly grown in large area of transition metal-coated Si substrates with high density. Each nanotube is terminated by transition metal cap, suggesting that the transition metals play an important role in the nanotube growth. Carbon nanotubes are curly in all cases, indicating the nanotubes to be defective due to very low growth temperature. Diameters and lengths of the nanotubes could be controlled by changing the ratio of methane to hydrogen and growth time. Raman spectum clearly shows the peak at 1592 cm-1 (G-band), indicating the formation of well graphitized carbon nanotubes.

NT+NS+EM+MS-WeP2 Nanoscale-controlled Handling of Carbon Nanotubes*, **O. Jaschinski**, P. Bernier, L. Vaccarini, C. Goze,* Universite Montpellier II, France*; G. Duesberg,* Trinity College Dublin, Ireland*; C. Journet, S. Roth,* Max-Planck-Institut fuer Festkoerperforschung Stuttgart, Germany

Carbon nanotubes are the most promising materials for applications in nanoelectronics and nanomechanics. For the determination of the electrical and mechanical properties of nanotubes and for the production of nanotube devices one needs the ability to handle nanoscale materials in a controlled way . We demonstrate how atomic force microscopy (AFM) can be used as a tool for manipulating and investigating carbon nanotubes. For an optimal use of AFM it is necessary to control the substrate-nanotube interaction. We present results of measurements of the mechanical properties of nanotubes obtained with various kinds of substrates. We show how the combination of lithography, manipulation by AFM and control of the adsorption process of nanotubes allow to prepare well defined sample configurations for very sophisticated measurements of the electrical and mechanical properties of carbon nanotubes. Based on these methods, techniques for the production of nanotube devices can be developed. This work was supported by European TMR contract NAMITECH ERBFMRX-CT96-0067 (DG12-MIHT)

NT+NS+EM+MS-WeP3 Aligned Carbon Nanotubes with Controlled Diameters Using Anodic Alumina Template*, **S.-H. Tsai**, H.C. Shih,* National Tsing Hua University, R.O.C.

The microwave plasma enhanced chemical vapor deposition (MPECVD) system had been successfully fabricated the well-controlled diameters of aligned carbon nanotubes on the anodic alumina template with a mixture of methane and hydrogen. Prier to test, the anodic alumina with pore arrays in various diameters were prepared by anodizing aluminum using oxalic, sulfuric, and phosphoric acid solutions. By adjusting the pore size of the anodic alumina, various carbon nanotube diameters can be obtained in a range of 30 to 100 nm and were examined by scanning electron microscopy and transmission electron microscopy.

NT+NS+EM+MS-WeP4 The Selective Growth of Aligned Carbon Nanotubes by PECVD Using Nickel Catalyst*, **H. Jeon**, K. Ryu, M. Kang,* Hanyang University, Korea

Carbon nanotubes have been studied extensively because of their own unique physical properties and also of their application potential for field emitters. One of the interesting applications is reported for display application, but neither industrial fabrication technology nor performance has been reported for practical display application. Here we tried to grow aligned carbon nanotubes selectively by plasma enhanced chemical vapor deposition (PECVD) method using nickel catalyst@footnote 1@ at temperatures below 600°C. These conditions for low temperature growths are suitable for field emission display which requires carbon nanotube emitters grown perpendicular to the Si substrate. In our experiment, a thin film of nickel(10-100nm) was deposited through a pattern mask on a Si substrate in UHV e-beam evaporator and was agglomerated by in-situ annealing for thirty minutes at 700°C. The use of a patterned catalyst enhanced the formation of selectively aligned nanotubes at low temperatures. After this process, Ni particles deposited on Si substrate were examined by AFM and SEM. Carbon nanotubes were selectively grown on Ni particle by PECVD with using the mixture of CH@sub 4@ and NH@sub 3@ at 600°C. In this process, CH@sub 4@ was used as the carbon source and NH@sub 3@ was used as a catalyst and dilution gas. During the process, many carboneous impurities can be produced and tried to eliminated by introducing H@sub 2@ plasmas. We examined the physical properties of carbon nanotubes by SEM, XRD and Raman spectroscopy. And we investigated the formation temperature of carbon nanotubes on silicon substrate and controlled the selective growth of aligned nanotubes. @FootnoteText@ @footnote 1@ Masako Yudasaka, et al.,Appl. Phys. Lett. 70(14), 7 April 1997.

Manufacturing Science and Technology Group
Room 611 - Session MS+PS-ThM

Environmentally Benign Manufacturing
Moderator: F. Shadman, University of Arizona

8:20am **MS+PS-ThM1 ESH as One of the Key Criteria for Semiconductor Process Development***, **A. Bowling**, T. Wooldridge, J. DeGenova, T. Yeakley, T. Gilliland, A. Cheng, L. Moyer,* Texas Instruments Inc. **INVITED**

During the development of advanced semiconductor devices, great benefit has been observed by treating ESH as a key process development specification. Earlier it had been feared that one must sacrifice process performance and/or cost to pursue ESH goals. However, in actuality, the process development engineer has frequently found that a process optimized for ESH also has better performance and lower cost per wafer. This paper will give a number of examples where ESH optimization has produced such performance and cost benefits. These examples include DI-water recycling, dilute SC1 wafer cleaning, wafer rinse optimization, dilute HMDS for resist develop, plasma-enhanced chemical vapor deposition (CVD) chamber cleaning optimization of PFC emissions, capture and recycling of copper plating solutions, copper CVD precursor recovery and recycling, post-metal etch solvent clean optimization, vacuum pump oil reclamation/optimization, and IPA recovery and recycling. The paper will conclude that ESH should be treated as another process performance and cost variable just like etch/deposition rate, non-uniformity, and particle counts.

9:00am **MS+PS-ThM3 The Environmental Impact of Perfluorinated Compounds used in the Semiconductor Industry***, **R.F. Jewett**,* Litmas Corp. **INVITED**

Perfluorinated compounds such as CF@sub 4@, C@sub 2@F@sub 6@, CHF@sub 3@, and others serve as low-toxicity carriers of fluorine for various semiconductor manufacturing processes. The low-toxicity of these chemically stable compounds make the workplace safer, but are a cause of concern when considering their long-term environmental impact. Most PFC's are strong absorbers of infrared radiation. This heat retention, combined with an extremely long atmospheric lifetime makes the environmental impact of continued emission significant and deserving of attention. This paper summarizes the current state of research on the roles of PFC's in the environment, and briefly considers various treatment methods that reduce emissions. There are several commercial systems available which have demonstrated dramatic performance in reducing PFC emissions.

9:40am **MS+PS-ThM5 Optimization of Processing Plasmas in the Semiconductor Industry for Minimal Environmental Impact***, **J.G. Langan**,* Air Products and Chemicals, Inc. **INVITED**

Most processing plasmas used by the semiconductor industry today have been extensively optimized for manufacturing performance. However, this optimization has traditionally not considered environmental impact as part of the performance criteria. Recent measurements have revealed that essentially all processing plasmas emit some form of gaseous by-products or un-reacted source materials which can be categorized as either volatile organic compounds (VOCs), hazardous air pollutants (HAPs), or perfluorinated compounds (PFCs). Although effective abatement solutions exist for some of these compounds they often transfer the problem from one phase to another requiring subsequent treatment. In an effort to develop truly optimized plasma processes we have investigated the operation of high pressure fluorinated gas (NF@sub 3@, C@sub 2@F@sub 6@) plasmas, predominantly used for CVD chamber cleaning applications, to determine which conditions lead to the highest throughput, lowest environmental impact processes. Using a variety of diagnostics; mass spectrometry, FTIR, electrical impedance analysis, and incident ion energy analysis the effect of operating conditions on etch rate, source gas utilization, by-product formation, and positive ion energy distribution functions have been determined. Using the insight gained from these measurements effective strategies have been identified to maximize the performance of CVD chamber cleans while minimizing their environmental impact. This presentation will give an overview of the environmental challenges associated with gaseous emissions from these tools and our efforts to identify viable solutions for chamber cleans in particular and semiconductor processing plasmas in general.

10:20am **MS+PS-ThM7 PFC Abatement in Inductively Coupled Plasma Reactors using O@sub 2@, H@sub 2@ and H@sub 2@O as Additive Gases@footnote 1@***, **X. Xu**, M.J. Kushner,* University of Illinois, Urbana

Perfluorinated compounds (PFCs), gases which have large global warming potentials, are widely used in plasma processing for etching and chamber cleaning. Due to under-utilization of the feedstock gases or by-product generation, it is usually necessary to abate emissions of PFCs from plasma processing reactors. Plasma abatement is being developed as one remediation strategy. Previous studies have shown that plasma abatement of, for example, C@sub 2@F@sub 6@ using O@sub 2@ as an additive may be effective in remediating the C@sub 2@F@sub 6@ but may also generate PFC products such as CF@sub 4@. Alternate additive gases may, however, avoid this problem. In this study, the scaling of plasma abatement is investigated using the 2-dimensional Hybrid Plasma Equipment Model (HPEM). Both the plasma etching chamber and downstream plasma burn-box are simulated in order to have realistic entry conditions for the burn-box. O@sub 2@, H@sub 2@, and H@sub 2@O are examined as additive gases in the burn-box. All PFCs in the effluent can generally be remediated in the burn-box at high power deposition with a sufficiently large flow of additive gases. In general CF@sub 4@ generation occurs during abatement of C@sub 2@F@sub 6@ using O@sub 2@ as an additive. CF@sub 4@ is not, however, substantially produced when H@sub 2@ or H@sub 2@O are used as additives due to the consumption of free fluorine by H, OH and H@sub 2@. The end products are dominated by COF@sub x@ with O@sub 2@ and by HF with H@sub 2@. The efficiency of PFC abatement (as measured by eV/molecule abated) decreases with increasing power and decreasing additive mole fraction. @FootnoteText@ @footnote 1@This work was supported by SRC and Applied Materials.

10:40am **MS+PS-ThM8 Modeling of Nonisothermal, Coupled Neutral/Plasma Dynamics in PFC Abatement Plasmas***, **M.W. Kiehlbauch**, A. Fiala, E.J. Tonnis, D.B. Graves,* University of California, Berkeley

Reducing PFC emissions is an area of increasing concern in semiconductor manufacture. One method of PFC emission reduction is through the use of point-of-use (POU) plasma abatement. In POU plasma abatement, an oxidizing species such as O@sub 2@ or H@sub 2@0 is added to the process tool effluent in the tool foreline. A plasma in the foreline is then used to convert PFCs to oxidized, wet-scrubbable species. Abatement plasmas can be used to reduce PFC emissions from oxide etch and in-situ CVD chamber clean processes and several commercial tools have been designed for these applications. Additionally, the abatement plasma structure is similar to downstream plasma sources which are increasingly used in chemical downstream etch and remote CVD chamber clean. A two-dimensional, coupled plasma and neutral model has been developed and applied to CF4/O2 and C2F6/O2 POU plasma abatement. The neutral model solves the overall neutral mass, momentum and energy balances. Additionally, the species mass balances are solved, together with a rigorous multi-component diffusion formulation. The neutral model is coupled via collisional terms to an INDUCT95 plasma model. The model allows the resolution of neutral temperature profiles and species concentration profiles. At high plasma powers, the neutral mean molecular weight decreases by ~ 50% while the neutral temperature increases by ~ 400%. The resulting density and velocity gradients have a major impact on the plasma structure and the composition of the gas flow leaving the plasma zone. We will present results that show these effects for various PFCs, power deposition profiles, flow rates, pressures and plasma powers. The relative importance of advective and diffusive transport will be considered. Additionally, the effect of wall temperature on the plasma structure will be investigated. Model results will be compared to those obtained experimentally. The application of these results to downstream plasma sources will be discussed.

11:00am **MS+PS-ThM9 Remote Plasma Sources for Cleaning CVD Reactors: Development and Implementation of a Technology for Green Manufacturing of Integrated Circuits***, **S. Raoux**, M. Sarfaty, T. Nowak, K.C. Lai, H.T. Nguyen, S. Thurwachter, J. Schoening, D. Silvetti, M. Barnes,* Applied Materials

The semiconductor industry is pursuing efforts to reduce emission of global warming PFC gases. Recently, a major advance in dielectric CVD (chemical vapor deposition) chamber cleaning has been introduced that virtually eliminates PFCs emissions from the process. Using NF@sub 3@ gas in a remote plasma source, the near complete dissociation of the gas achieves both superior chamber cleaning performance and improved environmental friendliness. In this paper, we will present experimental data (Mass and IR spectroscopy, Optical Emission Spectroscopy) used to identify the major phenomena related to the destruction of NF3 molecules, the generation of reactive (F) species, the recombination of atomic fluorine into F2 molecules and the efficiency of (SiO2, SiN,...) deposition residue removal. We will review the design requirements for this Remote Clean@super TM@ technology with respect to environmental and process performance, manufacturability, integration to the CVD process tool, and energy efficiency. An environmental (EnV) analysis was conducted, based on a process architecture framework, manufacturing process modeling, and multi-dimensional characterization. The EnV analysis integrates ESH impacts, manufacturing costs, and process performance measurements into a larger systems view with dynamic process models, established business processes, and an upstream design approach. The analysis methodology is presented along with a case study to compare an in situ C2F6-based RF clean with the Remote Clean@super TM@ technology.

11:20am **MS+PS-ThM10 Study of NF@sub 3@-Based High Density Plasma Oxide Etch Processes for Reduced Global Warming Emissions***, L.C. Pruette, S.M. Karecki, R. Chatterjee, R. Reif,* Massachusetts Institute of Technology

Current oxide etch processes in the semiconductor industry rely on fluorocarbon chemistries, particularly perfluorocarbons (PFCs). The emission of PFCs from these processes has become a cause of concern to the industry because of the long atmospheric lifetimes and the suspected global warming properties of these molecules. Whereas it has been seen that the use of some fluorocarbon molecules in place of PFCs does lead to measurable emissions reductions, stemming typically from a more efficient breakdown in the plasma that that seen with PFCs, it is also known that any process based on a fluorocarbon source material, whether a PFC or not, is likely to emit significant quantities of CF@sub 4@, an extremely long-lived molecule possessing an appreciable global warming potential. The goal of the research presented here is to minimize the amount of CF@sub 4@ and other PFC by-products produced in high density plasma (HDP) oxide etch processes by replacing the fluorocarbon etch gas with an inorganic molecule, namely NF@sub 3@. The NF@sub 3@ gas acts as a fluorine source for the plasma, and is mixed with a rare gas diluent to enhance plasma stability. Experiments illustrating the etch behavior of this dilute NF@sub 3@ plasma with the addition of several different hydrocarbon additives meant to enhance photoresist selectivity and sidewall passivation, and scavenge free fluorine, will be discussed. Scanning electron micrographs (SEMs) will be shown to demonstrate process feasibility. In-situ optical emission spectroscopy data will be used to characterize the plasma, and quadrupole mass spectrometry (QMS) and Fourier-transform infrared (FTIR) spectroscopy data will be used to identify the global warming compounds and hazardous air pollutants (HAPs) found in the process effluent.

11:40am **MS+PS-ThM11 Environmentally Harmonized Silicon Oxide Selective Etching Process Employing Novel Radical Injection Technique***, **K. Fujita**[1], S. Kobayashi, M. Hori, T. Goto,* Nagoya University, Japan*; M. Ito,* Wakayama University, Japan

Dry etching of silicon oxide (SiO@sub 2@) films is an essential process for fabricating deep contact holes in ultra large-scale integrated circuits (ULSIs). This process has been developed by using high-density plasmas employing stable fluorocarbon feed gases such as CF@sub 4@, C@sub 4@F@sub 8@ and so on. Fluorocarbon gases, however, cause a serious environmental problem, namely global warming and hereby the production of fluorocarbon gases would be restricted. Recently, we proposed a novel radical injection technique using a fluorocarbon radical source replacing stable fluorocarbon feed gases for preventing global warming, where polytetrafluoroethylene (PTFE) is ablated by a CO@sub 2@ laser and the generated fluorocarbon species (C@sub x@F@sub y@) such as reactive radicals are injected into the plasma reactor from externally. This technique, therefore, enables us to achieve a new plasma chemistry and a high-efficiency abatement due to the high exhaustion efficiency of reactive radicals coming from the plasma reactor compared with the stable gases. In this study, this system has been successfully applied to high-density plasma etching of SiO@sub 2@ over Si process and CF@sub x@ (x=1-3) radical densities in the plasma were evaluated by infrared diode laser absorption spectroscopy (IRLAS). A permanent magnet ECR plasma source which is very compact in size and easily scaled up to the large wafer size (~30 mm@phi@) was employed. The ECR zone was set about 6.5 cm above substrates. The Etching rate of SiO@sub 2@ and selectivity (SiO@sub 2@/Si) were 650 nm/min and 8, respectively at a microwave power of 400 W, a pressure of 6.5 Pa, a flow rate of 80 sccm and a bias voltage of -450 V in the ECR plasma employing the novel radical injection technique. These results indicate good characteristics compared with the conventional electromagnet ECR plasma. The etching mechanism are discussed on the basis of the behaviors of CF@sub x@ (x=1-3) radicals measured by the IRLAS.

Topical Conference on Emerging Opportunities and Issues in Nanotubes and Nanoelectronics
Room 6C - Session NT+NS+EM+MS-ThM

Nanotubes: Nanoelectronics and Field Emission

Moderator: N.J. Halas, Rice University

8:20am **NT+NS+EM+MS-ThM1 Carbon Nanotube Molecular Electronics***, **C. Dekker**,* Delft University of Technology, The Netherlands **INVITED**

I will present various recent results from electron transport measurements and scanning-probe microscopy on individual single-wall carbon nanotubes. Our early electrical transport work showed mesoscopic signatures at cryogenic temperatures. Additionally, a room-temperature transistor based on an individual semiconducting nanotube was established. Recent results in transport studies include first measurements on samples with low-ohmic contacts. The nanotubes are found to sustain very high current densities (~10^9 A/cm^2). I will show first measurements on kinked nanotubes, which act as an ontube intramolecular junctions. If time allows I may also present our results on AFM manipulation of nanotubes, and electrical measurements on manipulated nanotubes.

9:00am **NT+NS+EM+MS-ThM3 Electrical Transport in Single-Wall Nanotube Rings: Coherence and Localization***, H.R. Shea, R. Martel, **Ph. Avouris**,* IBM T.J. Watson Research Center

Understanding electrical transport in carbon nanotubes is essential for their possible use in nanoelectronics. Furthermore single-walled carbon nanotubes (SWNTs) provide ideal model systems on which to test theories of transport phenomena in 1D-systems. Linear SWNTs, however, do not have self-folding electron trajectories which can enclose magnetic flux. Thus, the technique of magneto-resistance (MR) cannot be applied directly to obtain information on the mechanism of electrical transport. Recently, we have developed a procedure by which linear SWNTs can be induced to form ring structures. Despite the high flexural rigidity of these materials, coils stabilized only by van der Waals forces can be produced in yields of ~50 %. These rings provide an ideal geometry for MR measurements. The MR is negative over the range of 0-5 T and from it we are able to determine the coherence length of the electrons in the rings. We found that over the entire range of 3 K - 60 K the SWNT-rings are in a state of weak localization induced by the constructive interference of electron waves propagating in opposite directions around the ring. Electric transport is not ballistic, and the coherence length reaches 520 nm at 3 K. From the temperature dependence of the coherence length we determine that the dominant dephasing mechanism at low T involves electron-electron interactions (Nyquist mechanism). Below ~1 K we observe an electronic phase transition to a strongly localized state. This transition is accompanied by the opening of a small energy gap and very strong MR and universal conductance fluctuations. An interesting zero bias anomaly (ZBA) is also observed below ~0.7 K. This ZBA is sensitive to magnetic fields and is ascribed to Kondo-type scattering from localized magnetic moments.

9:20am **NT+NS+EM+MS-ThM4 Analysis of Carbon Nanotube Field-Effect-Transistors (FETs)***, **T. Yamada**,* NASA Ames Research Center

Recent experiments on carbon nanotube FETs@footnote 1@ are analyzed theoretically. Comparing to the familiar Metal-oxide-semiconductor (MOS) FET characteristics, two qualitatively different behaviors can be pointed out:@footnote 1@ (1) the channel conductance g@sub d@ as a function of gate voltage V@sub g@ is not linear but somehow saturates, and (2) the drain current I@sub d@ does not saturate with the drain voltage V@sub d@ but rather monotonically increases. As for g@sub d@(V@sub g@), a staircase-like curve is expected with possible rounding. Each time the Fermi energy crosses a degenerate new subband, the nanotube conductance increases by double the quantum conductance, and thus g@sub d@ forms steps. When moving up to a next step, one new additional degenerate subband needs to be filled in the inversion layer, where larger V@sub g@ has to be applied. This will be a mechanism for the g@sub d@ saturation. The absence of I@sub d@(V@sub d@) saturation is due to the infrequent inelastic scattering by phonons or other carriers in the channel, regardless of the frequent elastic scattering by defects or impurities determining the small g@sub d@ (1/g@sub d@ ~ 2.9 M@ohm@).@footnote 1@ Carriers are not thermalized in the channel without efficient inelastic scattering,

[1] **PSTD Coburn-Winters Student Award Finalist**

resulting in no channel pinch-off formation and no I@sub d@ saturation. These reflect the nanotube electronic properties. We need to take them into account in the future device/circuit design, and develop a scheme best suitable for nanotube FETs. @FootnoteText@ @footnote 1@S.J. Tans, R.M. Verschueren & C. Dekker, Nature, 393, 49 (1998); R. Martel, T. Schmidt, H.R. Shea, T. Hertel, Ph. Avouris, Appl. Phys. Lett. 73, 2447 (1998).

9:40am **NT+NS+EM+MS-ThM5 Novel Length Scales in Nanotube Devices***, **F. Léonard**, J. Tersoff,* IBM T.J. Watson Research Center

We calculate the properties of p-n junctions, n-i junctions, and Schottky barriers made on a single-wall carbon nanotube. In contrast to planar bulk junctions, the depletion width for nanotubes varies exponentially with inverse doping. In addition, there is a very long-range (logarithmic) tail in the charge distribution, extending over the entire tube. These effects can render traditional devices unworkable, while opening new possibilities for device design. Our general conclusions should apply to a broad class of nanotube heterojunctions, and to other quasi-one-dimensional ``molecular wire" devices.

10:00am **NT+NS+EM+MS-ThM6 Field Emission from Carbon Nanotubes and Its Application to Electron Sources in Display Elements***, **Y. Saito**,* Mie University, Japan*; S. Uemura,* Ise Electronics Corp., Japan **INVITED**

Carbon nanotubes posses the following properties favorable for field emitters: (1) high aspect ratio, (2) small radius of curvature at their tips , (3) high chemical stability and (4) high mechanical strength. Field emission microscopy was carried out for both multiwall nanotubes (MWNTs) and single-wall nanotubes (SWNTs) produced by arc discharge between carbon. Four kinds of nanotubes were investigated; viz., (1) as-grown MWNTs prepared in the helium arc (called "pristine MWNTs"), (2) as-grown MWNTs in hydrogen ("nanog rafibers"), (3) purified MWNTs with open ends ("purified MWNTs" or "open MWN Ts"), and (4) purified SWNTs. Field emission patterns as well as current versus voltage characteristics and Fowler-Nordheim plots for respective nanotubes will be discussed. As an application of nanotube field emitters, we manufactured cathode-ray tube (CRT) type lighting-elements and vacuum-fluorescence display (VFD) panels. In both display elements, conventional thermionic cathodes were replaced with MWNT field emitters which were fixed onto a stainless steel cathode by using conductive paste. In CRT-type lighting elements, the nanotube cold cathode was covered with a grid electrode, the gap between the cathode and the grid being in a range from 0.2 to 0.7 mm. Current density on the cathode surface was on the order of 10 - 100 mA/cm@super 2@ at an average field strength of 1.5 V/ µm. Luminance of the phosphor was intense enough for practical use; e.g., 6.3x10@super 4@ cd/m@super 2@ for green light at an anode current of 0.2 mA and an anode voltage of 10 kV. A direct-current driving test revealed a lifetime over 10,000 hours.

10:40am **NT+NS+EM+MS-ThM8 Emission Properties of Large-area, Fully-sealed Carbon Nanotube Field Emission Display***, **W.B. Choi**, H.Y. Kim, D.S. Chung, J.H. Kang, I.T. Han, J.M. Kim,* Samsung Advanced Institute of Technology, Korea

Fully sealed field emission display (FED) in size of 4.5 inch has been fabricated by using carbon nanotubes. Carbon nanotubes were fabricated by arc discharge technique. Carbon nanotube aligning techniques with the aid of slurry squeezing and electrophoresis were used for making large-area cathode. The Y@sub 2@O@sub 2@S:Eu, ZnS:Cu,Al, and ZnS:Ag,Cl, phosphors are deposited on the anode glass for red, green, and blue colors, respectively. The assembled structure was sealed in an atmosphere of highly purified Ar gas by means of a glass frit. The display plate was evacuated down to the pressure level of 1x10@super -7@ Torr. Three non-evaporable getters of Ti-Zr-V-Fe were activated during the final heat-exhausting procedure. Finally, the active area of 4.5-inch panel with fully sealed carbon nanotubes was produced. The turn-on field for lighting phosphor was 1.5 V/µm. Brightness of over 1000 cd/m@super 2@ at 4V/µm was achieved on the entire area of 4.5-inch panel from the green phosphor-ITO glass. The fluctuation of the current was satisfied for the field emission display. These reliable results enable us to produce carbon nanotube-based large area full-color FEDs in the near future. In this presentation, fabrication techniques and emission properties of large area carbon nanotube FED will be demonstrated.

11:00am **NT+NS+EM+MS-ThM9 The Structure of Nanotubes Observed with Thermal Field Emission***, **K.A. Dean**, B.R. Chalamala,* Motorola Flat Panel Display Division*; O. Groening, O.M. Kuettel,* University of Fribourg, Switzerland

We studied the structure of single-walled nanotubes (SWNTs) using field emission microscopy. The field emission images obtained after thermal cleaning depict the spatially-resolved electronic structure of the individual SWNT caps. Using high temperature field emission, we demonstrate how to distinguish between the patterns of individual SWNTs and those of clusters, how to alter the structure of the nanotube cap, and how to extract information about the SWNT structure and chirality from the field emission image. In addition, we demonstrate a technique for measuring the SWNT local density of states through thermal field emission energy distribution measurements. With this technique, we observe that nanotubes have discrete electronic states several eV above the Fermi level, and we suggest that these states are responsible for the large variation in emission current vs. temperature behavior observed among nanotubes.

11:20am **NT+NS+EM+MS-ThM10 Fabrication and Field Emission Properties of Adherent Carbon Nanotube Films***, **C. Bower**,* University of North Carolina at Chapel Hill*; W. Zhu, G. Kochanski, S. Jin,* Bell Laboratories, Lucent Technologies*; O. Zhou,* University of North Carolina at Chapel Hill

We report on the fabrication and field emission properties of carbon nanotube films. Films of randomly oriented carbon nanotubes were deposited onto substrates using a variety of techniques. The nanotube films exhibited stable field emission current at low turn-on fields (electric field needed to generate 1 nA of current) and threshold fields (electric field needed to generate 10 mA/cm@super 2@). A single-walled carbon nanotube film with approximately 20% surface coverage showed a turn-on field of 1-1.2 V/µm and a threshold field of 1.3-1.7 V/µm. The emission characteristics deviated from typical Fowler-Nordheim behavior at high current densities. The nanotube films were capable of generating large current densities (> 4 A/cm@super 2@). The emission properties were found to be stable over several days of emitting at 10 mA/cm@super 2@. The emission site density of the films was measured to be 10@super 4@-10@super 5@ sites/cm@super 2@ and the emission patterns were studied.

11:40am **NT+NS+EM+MS-ThM11 Characterization of Oriented Carbon Nanotube Cathodes for Field Emission Flat Panel Display and Light Source Applications***, **N.N. Chubun**,* SRPC Istok, Friazino, Russia*; A.G. Chakhovskoi, C.E. Hunt,* University of California, Davis*; A.N. Obraztsov,* Moscow State University, Russia

Oriented carbon nanotubes were recently reported as a viable material for fabrication of field emission cathodes applicable to flat panel displays and vacuum light sources.@footnote 1@ Field emission properties of diode and triode structures with oriented nanotube cathodes were studied in DC-mode in ultra-high vacuum chamber and in sealed glass prototype devices. Cathodes of 9x9mm grown using glow-activated direct current discharge CVD method on molybdenum and single crystal silicon substrates were studied at currents up to 2 milliamps using metal or phosphor coated anodes. The nanotubes exhibited various degrees of initial surface orientation depending on parameters of the deposition process. An additional orientation of the nanotubes in electric filed during first activation of the cathodes was observed. Monochrome low-voltage FPD phosphors were used for cathodoluminescent brightness/light efficiency characterization and for monitoring of distribution of the filed emission sites. Turn-on voltages varied from 1 to 5 V per micron depending on the extraction electrode configuration. Influence of vacuum conditions and initial training on stability and lifetime of the cathodes was studied. I/V characteristics of the nanotube cathodes were directly compared to those of carbon fiber and carbon foam emitters and to diamond-coated field emission arrays showing potentially greater reproducibility and uniformity of filed emission of the oriented nanotube cathodes. @FootnoteText@ @footnote 1@ A.N.Obraztsov, I.Yu.Pavlovsky, A.P.Volkov, V.L.Kuztetsov, A.L.Chuvilin. MRS 1999 Spring Meeting, San Francisco, CA, April 1999, p.B.4.9/C.2.9.

Topical Conference on Emerging Opportunities and Issues in Nanotubes and Nanoelectronics
Room 6C - Session NT+NS+EM+MS-ThA

Nanotubes: Functionalization and Metrology

Moderator: D. Herr, Semiconductor Research Corporation

2:00pm **NT+NS+EM+MS-ThA1 Opportunities and Challenges for Nanotubes in Future Integrated Circuits**, ***R.R. Doering,*** Texas Instruments **INVITED**

We speculate about a few potential research opportunities that may be of mutual interest to both the microelectronics and nanotube communities. Perhaps the most evolutionary use of nanotubes in integrated circuits would be in the form of "thin films." Such use would capitalize on "bulk" material properties. For example, a layer of nanotubes (with "best metallic" conductivity) might serve as an interconnect film. Alternatively, an insulating nanotube layer (e.g, "modified" CNTs or other tube chemistries) might be used as a low-K dielectric. Even lower K might be achieved by using high-conductivity CNTs as "self-supporting wires," taking advantage of their inherent mechanical strength to eliminate the need for solid insulating layers. Another type of evolutionary use might involve nanotube structures for passive IC components. For example, the huge volume density of surface area looks appealing for DRAM capacitors. A significant amount of current nanotube research is aimed at active devices, which might ultimately replace today's silicon semiconductor switches. One of the most exciting prospects is the potential for more extensive and effective use of the "third-dimension" in integrated circuits. However, as with today's "planar" IC technology, the benefit/cost of "going 3D" will depend on details of the practical fabrication techniques. For nanotubes, this brings up "formation/place/route" issues. Nanotubes may also play a role in future "atomically perfect manufacturing," which may be needed to scale much below about 50-nm features regardless of the type of device technology employed.

3:00pm **NT+NS+EM+MS-ThA4 Simulations of Plasticity and Kink Catalyzed Functionalization of C and BN Nanotubes**, ***D. Srivastava,*** NASA Ames Research Center; *M. Menon,* University of Kentucky

Routes to plasticity and kink catalyzed chemistry for functinlaization of C and BN nanotubes are investigated via classical molecular dynamics (MD) and generalized tight-bonding quantum molecular dynamics (QMD) methods. The critical strain for plasticity of BN nanotube is found to be more than that for the similar C nanotube. The structural collapse of nanotubes under compression is explored in which we find that the accumulated strain drives the tube in a plastic deformation in which four-fold coordinated tetrahedral bonds form at the location of the collapse. This lowers the elastic limit of compressed nanotubes to much less than what was predicted earlier with classical MD potential methods alone.@footnote 1@ The critical stress needed for this transition, as computed with QMD method, is in good agreement with experimental values observed for compressed nanotubes in polymer composites and graphite to diamond like transition in a bucky-onion pressure cell. Mechanical kink driven side-wall functionalization of C and BN nanotubes is also explored. We find that mechanical twisting and bending of the tube enhances the binding energy (and lowers the cohesive energy) at kink or edge sites by 1-2 eV as compared to the reactivity of undeformed tubes. Highly localized selective functionalization and etching of sidewalls could thus be possible through kink catalyzed chemical reactivity of nanotubes. A preliminary example of the experimental evidence will be shown.@footnote 2@ @FootnoteText@ @footnote 1@D. Srivastava, M. Menon, and K. Cho, submitted (1999). @footnote 2@D. Srivastava, D. W. Brenner, J. D. Schall, K. D. Ausman, M. F. Yu and R. S. Ruoff, to appear J. Phys. Chem. (1999).

3:20pm **NT+NS+EM+MS-ThA5 Nanoindentation and Nanotribology with Carbon Nanotubes**, *B. Ni, A. Garg,* ***S.B. Sinnott,*** University of Kentucky

The mechanisms by which carbon nanotubule (CNT) proximal probe tips deform during the nanometer-scale indentation and scratching of surfaces are explored using classical molecular dynamics simulations. The forces acting on the atoms in the simulations are calculated using a many-body, reactive bond-order potential for hydrocarbons. The results show that single-walled and multiwalled CNT tips indented against hydrogen-terminated diamond and graphene surfaces buckle and slip to relieve the applied stress. However, in the case of reactive surfaces, tip-surface adhesion occurs on contact that ultimately destroys the tubule. Furthermore, while shell-shell interactions have little effect on the deformation mechanisms, the multiwalled tubule is stiffer than comparably sized single-walled tubules. Finally, the way in which the deformation of these tubules changes during scratching of diamond and graphene surfaces will be discussed and the results compared to available experimental data. @FootnoteText@ Supported by NASA Ames Research Center (NAG 2-1121) and NSF MRSEC (DMR-9809686).

3:40pm **NT+NS+EM+MS-ThA6 Quantum Chemistry Study of Carbon Nanotube Fluorination**, ***R.L. Jaffe,*** NASA Ames Research Center

Quantum chemistry calculations are carried out to characterize the products of fluorination reactions of C@sub 60@, C@sub 70@ and carbon nanotubes. The calculations utilize density functional theory with a widely used hybrid nonlocal functional (B3LYP-DFT). C@sub 60@ is known to readily undergo reaction with molecular fluorine to form C@sub 60@F@sub n@ with n<44. C@sub 60@F@sub 18@ and C@sub 60@F@sub 36@ are the predominate products. C@sub 70@ also is known to undergo similar reaction, but the products have not been completely characterized. Less is known about the possibility of fluorinating nanotubes. However, it has been conjectured that highly fluorinated nanotubes may have attractive chemical and dielectric properties. Fluorination of C@sub 60@ and C@sub 70@ is used to benchmark the calculations for nanotubes. Previous studies have demonstrated that polycyclic aromatic hydrocarbons with an externally constrained curvature are good model molecules for studying the functionalization reactions of single-walled carbon nanotubes. Reaction is likely if the products are energetically stable and any activation energy barriers are small. Initial studies for C@sub 60@ and (10,10) nanotubes have shown that the difluoronated products are quite stable and the fluorination reaction is highly exothermic.

4:00pm **NT+NS+EM+MS-ThA7 Gear-like Rolling Motion of Carbon Nanotubes on HOPG**, ***M.R. Falvo,*** *J. Steele, A. Buldum,* University of North Carolina, Chapel Hill; *D. Schall,* North Carolina State University; *R.M. Taylor II,* University of North Carolina, Chapel Hill; *D.W. Brenner,* North Carolina State University; *J. Lu, R. Superfine,* University of North Carolina, Chapel Hill

Though much work has been done in recent years in exploring nanometer and atomic scale sliding friction, little experimental or theoretical work has been done on rolling and its relation to sliding at this scale. We will present lateral force microscope investigations of frictional phenomena of multiwall carbon nanotubes (MWCNTs) on highly oriented pyrolytic graphite (HOPG), that include all the rigid body motions: sliding, rotating in-plane, and rolling. Using an advanced manipulation interface for AFMs, the nanoManipulator, we study these friction phenomena through sophisticated manipulation experiments where lateral forces are monitored during manipulations. We have manipulated MWCNTs into a state of atomic registry between the lattice of the tube and underlying substrate. Out of atomic registry the friction is smooth and uniform. As the CNT is rotated in the plane of the substrate, three discrete atomically registered orientations are observed marked by a 3-10 fold increase in the lateral force required to remove them from these orientations. Results of molecular statics calculations for this system show that the potential energy as a function of in-plane rotation angle has three deep minima spaced sixty degrees apart corresponding to atomic lattice registry. When the CNT locks into atomic registry, there is a transition from an in-plane rotational motion to a stick-slip rolling motion. Rather than being perfectly cylindrical, our lateral force data during rolling indicate that the CNT may be faceted (polygonal cross section). MS calculations indicate that faceting is to be expected for MWCNT depending on diameter and wall thickness. The calculated friction expected for rolling a faceted MWCNT agrees well with experimental lateral force data. Molecular dynamics calculations will be shown that lend insight into the energy loss mechanisms for both the sliding and rolling case. This work is supported by the NIH (NCRR), NSF, ONR (MURI), and ARO (DURIP).

4:20pm **NT+NS+EM+MS-ThA8 Selectivity and Diffusion of Binary Fluids in Carbon Nanotubes**, ***Z. Mao,*** *S.B. Sinnott,* University of Kentucky

Carbon nanotube bundles have been proposed as good materials for the manufacture of tailored ultrafiltration membranes due to their uniform, porous structure. In contrast to conventional membranes produced by only partially sintering a ceramic or stretching a polymer, a nanotube membrane would offer the advantages of fewer blocked pores and a narrower distribution of pore sizes. To investigate the properties of a nanotube membrane, the adsorption of simple binary fluids within single tubules and tubule bundles are modeled using atomistic simulations. Specifically, classical molecular dynamics simulations are performed using a combined many-body, reactive bond-order and Lennard-Jones potential. The results show how the diffusion of these molecules proceeds at differing rates within the nanotubes as a function of the diameter and helical structure of the tubules, the density of the fluid, the size difference between the molecules, and temperature. An example of a binary fluid that has been studied is a mixture of CH@sub 4@ and C@sub 4@H@sub 10@ at room temperature. The simulations predict high selectivity in the diffusion of these molecules through the nanotubes. They also allow for the determination of the type of diffusion followed by each type of fluid molecule. Comparisons will be made between these simulation results and the results of similar studies in the literature of diffusion in zeolites and other molecular sieves. @FootnoteText@ Supported by NASA Ames Research Center (NAG 2-1121) and NSF MRSEC (DMR-9809686).

4:40pm **NT+NS+EM+MS-ThA9 Improved Tungsten Disulfide Nanotubes as Tips for Scanning Probe Microscopy***, **A. Rothschild**, G. Frey, M. Homyonfer, M. Rappaport, S.R. Cohen, R. Tenne,* Weizmann Institute of Science, Israel

Synthesis and applications of long and hollow WS@sub 2@ nanotubes are described. Although synthesis of nanotubes from various inorganic compounds have been reported, the high yields of uncontaminated nanotubes reported here represents a significant improvement over past efforts by ourselves and others.@footnote 1@,@footnote 2@ The nanotubes are synthesized in a two-step process the first being the creation of WO@sub 3@ nanoparticles by heating a tungsten filament in the controlled presence of water. The second step, sulfidization, resulted in a 30 times increase in the length of these particles without change in width so that nanotubes up to 10 microns in length and 20-40 nm width were formed. These tubes were attached to scanning force microscope (SFM) tips and used to image deep and sharp features inaccessible by sharp silicon tips. Due to their sandwich S-W-S structure, these nanotubes are probably stiffer than the carbon analogs and hence less prone to instabilities under such rigorous scanning conditions. We propose application of these probes for nanophotolithography, aided by the facile excitation of these compounds by visible and infra-red light. Support by the Israel Ministry of Science, Israel Science Foundation, and Applied Materials-Weizmann Foundation are gratefully acknowledged. A.R. is a recipient of the Lavoisier fellowship (France). @FootnoteText@ @footnote 1@ Y. Feldman, E. Wasserman, D.J. Srolovitz, R. Tenne, Science 267, 222 (1995). @footnote 2@ N.G. Chopra, et al, Science 269, 966 (1995).

Topical Conference on Emerging Opportunities and Issues in Nanotubes and Nanoelectronics
Room 6C - Session NT+NS+EM+MS-FrM

Nanotubes: Growth, Characterization and Properties II
Moderator: R.L. Jaffe, NASA Ames Research Center

8:20am **NT+NS+EM+MS-FrM1 Gas-phase Nanotube Production at High Pressure By Disproportionation of Carbon Monoxide**, ***P. Nikolaev,*** G. B. Tech Inc. / NASA - JSC*; M. Bronikowski, K. Bradley, D. Colbert, K. Smith, R.E. Smalley,* Rice University

Single-wall carbon nanotubes (SWNTs) were produced in gas phase, in a flow tube reactor in 3 - 15 atm. of CO at 850@super o@ - 1200@super o@C. Nanotube growth was catalyzed by unsupported iron particles created in-situ by decomposition of iron pentacarbonyl vapor which was added to the CO feedstock at a few ppm level. We find that low Fe(CO)@sub 5@ concentration combined with fast heating rate of feedstock gas allows us to produce very small iron particles, while high pressure increases the rate of CO disproportionation, leading to effective nucleation and growth of SWNTs. Unlike pyrolysis of hydrocarbons, CO disproportionation is a "clean" process which proceeds only on the catalyst surface, resulting in essentially no amorphous carbon overcoating. Diameter distribution of the SWNTs is rather narrow and depends on CO pressure. Higher CO pressures (10 atm.) yield smaller nanotubes, with distribution centered at 0.7 nm (which is roughly the size of C@sub 60@ molecule). Nanotube yield relative to the amount of iron catalyst increases as the heating rate and mixing of Fe(CO)@sub 5@ are enhanced, indicating better catalyst utilization. In order to further increase nanotube yield, we have designed a "shower head" injector, in which cold CO/Fe(CO)@sub 5@ feedstock enters furnace through water-cooled injector, surrounded by "shower head" carrying CO pre-heated to 1200@super o@. Nanotube yield is also increased by addition of small amount of methane, while more CH@sub 4@ results in amorphous overcoating on the nanotube surface. In contrast to previously reported SWNT production methods, this scheme constitutes a continuous flow gas phase SWNT production process. It should therefore be readily amenable to scale up for bulk SWNT production.

8:40am **NT+NS+EM+MS-FrM2 The Optical Properties of Carbon Nanotubes and Their Use in the Characterisation of Bulk SWNT Material**, ***M.S. Golden***, *T. Pichler, R. Friedlein, M. Knupfer, J. Fink,* IFW Dresden, Germany*; O. Jost, A.A. Gorbunov, W. Pompe,* TU Dresden, Germany

The investigation of the optical properties of carbon nanotubes,@footnote 1,2@ either using UV-Vis or electron energy loss spectroscopies, offers insight into carbon nanotubes on two levels. Firstly, analysis of the energy positions of the characteristic electronic transitions between the singularities in the density of states enables a quick and easy determination of the overall NT yield, the diameter distribution and the ratio of semiconducting-to-metallic SWNTs in bulk samples. This represents an ideal express characterisation method to accompany tuning of the nanotube preparation process parameters. Secondly, the momentum dependence of the collective excitations of the @pi@-electron system in nanotubes measured using high resolution electron energy loss spectroscopy in transmission proves to be a sensitive probe of the effective dimensionality of the electron system and inter-tube interaction, both in bulk samples of SWNT and MWNT. @FootnoteText@ @footnote 1@ T. Pichler, M. Knupfer, M. S. Golden, J. Fink, A. Rinzler, R. E. Smalley, PRL 80 4729 (1998) @footnote 2@ T. Pichler, M. Sing, M. Knupfer, M. S. Golden, J. Fink, Solid State Commun., 109, 721 (1999).

9:00am **NT+NS+EM+MS-FrM3 Li Intercalated Carbon Nanotubes Ropes**, *J. Lu, J. Zhao,* ***A. Buldum****, B. Gao, O. Zhou,* University of North Carolina, Chapel Hill **INVITED**

The electronic and electrochemical properties of Li intercalated single-wall nanotube ropes are studied theoretically using ab initio method@footnote 1@ and experimentally in an electrochemical cell.@footnote 2@ Complete charge transfer is found between Li atoms and nanotubes. The energetic and electrochemical potential of intercalated Li atoms on both the inside and the outside of tubes are investigated. The intercalated ropes are metallic with conduction band resides on C atoms. Both theoretical and experimental studies suggest that it is possible to achieve a Li intercalation density significant larger than that in the graphite, making the Li intercalated nanoropes a promising material for battery applications. @FootnoteText@ @footnote 1@ J. Zhao, A. Buldum, J. P. Lu, to be published. @footnote 2@ B. Gao and O. Zhou, to be published.

9:40am **NT+NS+EM+MS-FrM5 Mechanical and Electronic Properties of Carbon Nanotubes Under Bending**, ***L. Yang****, M.P. Anantram, J. Han, R.L. Jaffe,* NASA

Bending, buckling and even collapsing of carbon nanotubes have been more frequently observed experimentally. They could be elastic or plastic deformations, and responsible for a variety of mechanical and electronic measurements. We systematically investigate mechanical and elecronical properties of carbon nanotubes under these deformations. They are correlated with tube configuration and stress - strain relations. Some interesting observations are made. For example, electron transport can be enhanced or suppressed, depending on the configuration and deformation of a tube. We also apply the simulation results in understanding some related experimental observations.

10:00am **NT+NS+EM+MS-FrM6 Effect of Strain on Electrical Properties of Carbon Nanotubes**, ***S. Paulson****, N. Snider, M.R. Falvo, A. Seeger, A. Helser, R.M. Taylor III, R. Superfine, S. Washburn,* University of North Carolina, Chapel Hill

We have used an advanced interface to an Atomic Force Microscope to apply strain to carbon nanotubes. Simultaneously, we measure the current voltage characteristics, and see how they change as a function of strain in the tube. We have applied enough strain to fracture nanotubes, causing the resistance to become infinitely large, and then reassembled the ends to form junctions. The characteristics of these junctions will be discussed, as well as other strain dependant effects.

10:20am **NT+NS+EM+MS-FrM7 Molecular Dynamics Simulation of the Thermal Conductivity of Carbon Nanotubes**, ***M.A. Osman,*** NASA Ames Research Center, US*; D. Srivastava,* NASA Ames Research Center

Carbon nanotubes (CNT) have very attractive electronic, mechanical, and thermal properties. Recently, measurements of thermal conductivity in single wall CNTs showed thermal conductivity magnitudes ranging from 17.5 to 58 W/cm-K at room temperature, which are better than bulk graphite.@footnote 1@ The cylinderical symmetry of CNT leads to large thermal conductivity along the tube axis which is an improvement over the strongly anisotropic nature of thermal conductivity of graphite. Additionally, unlike graphite, CNTs can be made into ropes that can be used as heat pipes. We have investigated the thermal concutivity of single wall CNTs Using non-equilibrium molecular dynamics (MD) with Brennar potential. The results of the simulation are in good agreement with the experimental results. We will discuss the results of our simluation and report on the effects of tube diameter and chirality on the thermal conductivity. @FootnoteText@ @footnote 1@ J. Hone, M. Whitney, C. Piskoti, and A. Zettl, Phys. Rev. B59, R2514 (1999).

10:40am **NT+NS+EM+MS-FrM8 Materials Applications of Carbon Nanotubes: Hydrogen Storage and Polymer Composites**, ***S.J.V. Frankland****, D.W. Brenner,* North Carolina State University

Simulations addressing two applications of carbon nanotubes will be presented. Nanotubes have been proposed as storage media for hydrogen in fuel cells. Experiments have shown that the nanotube samples contain more hydrogen than will fit densely packed into the tubules themselves. Therefore, the location of the hydrogen is in question. The Raman shift of the hydrogen may provide a useful indicator of its placement. So far, two qualitative trends have been identified with molecular dynamics simulation which should enable the distinction of internal versus intercalated hydrogen. For internal hydrogen a decreasing Raman shift is observed with increasing nanotube radius. For intercalated hydrogen, the simulations predict a broadened Raman band with relatively little dependence on nanotube radius. The second application being considered is the usage of nanotubes to strengthen polymer composites. Molecular dynamics simulations are in progress to understand the load transfer mechanism between the polymer and the nanotube.

Author Index

Bold page numbers indicate presenter

Author Index