Incorporating Principles of Industrial Ecology
Room 304 - Session IE-TuM

Methods of Industrial Ecology Analysis / Global Concerns

Moderator: R.L. Bersin, Ulvac Technologies, Inc.

9:00am **IE-TuM3 The 21st Century Co-Evolution of Technology and Environmental Science*, T.E. Graedel,*** Yale University **INVITED**

Technology, traditionally seen as the enemy of the environment, is likely to be a positive environmental force in the 21st century, and not only through its application to feed the 8-12 billion people that will occupy the planet. Technology is also likely to be central to improving overall quality of life. Nevertheless, 21st century technology will have to consider the potential environmental impacts of its every action. The process of so doing, termed industrial ecology, is rapidly entering planning, product design, and customer response activities throughout the world. Industrial ecolgoy works in cooperation with environmental science, and incorporates new environmental knowledge in its decision-making processes. The tools of industrial ecology, including life-cycle assessment, design for environment, and materials flow analysis reveal that the potential benefits to both corporations and the environment of optimizing technology-environment interactions are substantial. Some examples of such optimization will be presented and discussed.

9:40am **IE-TuM5 Single Particle Analysis of Particulate Pollutants in Yellowstone National Park and Hawaii Volcanoes National Park*, R.E. Peterson,*** *B.J. Tyler,* Montana State University

Particulate pollution is a complex mixture of organic and inorganic compounds which includes a wide range of sizes and whose composition can vary widely depending on the time of year, geographical location, and both local and long range sources. Particles greater than 2 micrometers in diameter are generally formed by mechanical processes while smaller particles are formed by gas to particle conversion and accumulation/coagulation. Because particles smaller than 2.5 micrometers can become trapped deep in the lungs, it is of particular interest to identify toxic substances, such as heavy metals and polyaromatic hydrocarbons, that may be present in particles of this size range. We are evaluating the potential for using TOF-SIMS to study the composition of single particles from atmospheric aerosol. For this study, samples of naturally occurring and anthropogenic atmospheric aerosol were collected at the west entrance to Yellowstone National Park (YNP) during the winter snowmobile season of 1998/99. During the winter snowmobile season, incomplete combustion products from snowmobile exhaust may be a predominant source of airborne particulate matter in YNP. In Hawaii Volcanoes National Park (HVNP), lava flows from the ongoing Kilauea volcano eruption are a particulate source which has been little investigated. Aerosol near fresh pahoehoe flows was sampled in January and May of 2000. Graseby/Anderson cascade impactors were used to collect size segregated fractions of the aerosol onto aluminum substrates in YNP and onto gold coated substrates in HVNP. Sections of the substrates have been imaged using a PHI TRIFT I instrument with a Ga primary ion source. Both positive and negative ion images have been studied. A large number of particles could be distinguished on the impactor surfaces. Multivariate methods, including mixture models and principal components analysis have been employed to enhance image resolution and aid in interpretation of the SIMS images.

10:00am **IE-TuM6 Environmental Concerns in Brazil*, T.M. Tavares,*** Federal University of Bahia (UFBA), Brazil **INVITED**

Brazil has not reached the phase of concern for industrial ecology. Society has not even been able to practice selection of solid wastes in a broad sense. Industries are now concerned on obtaining ISO14000 certificate and adopting clean technologies. In a capitalist society the main driving force is economic interest. The means available to society to protect the environment are government regulation/ law enforcement and consumers demand. In Brazil the frame of the legislation for environmental management is closer to that of Europe than of USA. It includes a good and often efficient system of licensing installation of new enterprises and operation of existing ones. A great number of large ecological reserves have been established. However two things are lacking: proper criteria for a great number of chemical pollutants and law enforcement. National consumer's demands have concentrated on protection of natural reserves and on industrial emission reduction. Demands of international consumers have resulted in cleaner production, as in pulp industries with change to elemental chlorine free (ECF) or total chlorine free (TCF). Brazil as a whole has no tradition in development of technologies. First, it lacks both financial and trained human resources since society never demanded it. This has also not been a concern of the government until 1999, when a new program for development of technologies has been launched ; Secondly, not before recently, part of the restricted development of technology in the country aimed green production. However, when government takes the initiative and demands new technology to meet economic interest, society responds. In 1970, 80% of the oil consumed in Brazil came from abroad, and the international prices were rising. With incentives from the Government, ethanol was introduced as fuel and new motors were development. Although the economic interest was the driving force, the environment profited from this less polluting fuel, and now other countries are adopting it. International demands can play an important role, and may be able to introduce carbon fixation through incentives, to more recycling, to assessment of life-cycle of products and to a greater environment conscious attitude.

10:40am **IE-TuM8 Multi-phase Atmospheric Chemical Processes: A Major Gap in Understanding Regional to Global Air Pollution Issues*, L. Barrie,*** Pacific Northwest National Laboratory **INVITED**

Chemicals from natural or anthropogenic activities that are released to the atmosphere as gases or particles are dispersed and transported on the winds. Their residence time and hence, range of influence, is determined by the processes of chemical and physical transformation, air-surface exchange and precipitation scavenging. Multi-phase chemistry involving interactions of gases with solids or liquids in the atmosphere or at the Earth's surface is often a major obstacle in understanding environmental chemical cycles and hence establishing effective pollution abatement strategies. There are a variety of pollution issues operating on a range of scales from local to global that threaten the quality of life on this planet. They include: urban smog (e.g. ozone and particulate matter), regional acidification/toxification and visibility reduction, global stratospheric ozone depletion and climate change. An understanding of multi-phase reactions is complicated by the largely unknown, highly variable nature of liquid/solid particles in the atmosphere. These include atmospheric aerosols (0.001 to 10 micrometers), cloud droplets and ice (1 to 20 micrometers) and rain/snow particles (20 to 20000 micrometers). They range greatly in composition and ionic strength (6x10@super -6@ to 10 molal). The interaction of gases with particles involves unreactive phase-partitioning processes as well as reactive kinetic processes. In the case of persistent semi-volatile substances such as herbicides, pesticides and polycyclic aromatic compounds, the environmental pathways are often dominated by the former process, In contrast, many substances are chemically produced or transformed during gas-particle interactions. There is a need to understand the nature of organic compounds in atmospheric particles and the basic physical chemistry of the interaction of these mixtures with water vapour and other gases.

11:20am **IE-TuM10 Structure and Composition of Size- and Time-Resolved Outdoor Aerosols Determined Using TOF-SIMS*, D.J. Gaspar,*** *M.A. Carpenter, J.P. Cowin, D.R. Baer,* Pacific Northwest National Laboratory

The study of aerosol particles has been identified as a top priority in atmospheric research due to their importance as heterogeneous reaction sites and the potential health consequences of particulate inhalation. Aerosols are known to have highly variable composition, with non-volatile, semi-volatile, and volatile organic and inorganic constituents. Although much work has been done recently, further understanding of structure and composition remains important. Thus, the composition of outdoor aerosols have been investigated using time-of-flight secondary ion mass spectrometry (TOF-SIMS). Particles were collected using a multiple stage impactor, which time tagged and sorted incident particles from 0.1 to 10 microns into discrete size ranges. A PHI TRIFT TOF-SIMS instrument was used with a Ga@super +@ liquid metal ion gun (LMIG) for both depth-profiling and analysis, and a Cs@super +@ ion source for more extensive depth-profiling. Mass spectra for both negative and positive secondary ions were obtained for the time- and size-sorted particles. Data was obtained for both collections of particles and a number of individual particles. The mass spectra have been analyzed to determine the inorganic and organic fractions of the aerosol particles. Three-dimensional molecular and atomic maps have been constructed for key environmentally important components of several characteristic particles. We relate the composition to environmental factors such as daylight and road traffic, and inferences are drawn concerning sample chemical history.

Incorporating Principles of Industrial Ecology
Room 304 - Session IE-TuA

Green Manufacturing

Moderator: P.M. Beauchamp, Jet Propulsion Laboratory

2:00pm **IE-TuA1 Challenges in Bringing Green Manufacturing Technologies to the Clean Room Floor*, S. Raoux,*** Applied Materials **INVITED**

The semiconductor industry is undertaking major research and development efforts to reduce the environmental impact of its manufacturing processes. In particular, technologies have been introduced to eliminate atmospheric emissions of global warming compounds, reduce solid waste and conserve energy and water resources. At each technology node, semiconductor fabrication processes are amenable to change, and implementation of sustainable manufacturing practices should be favored. However, the stringent requirements of the semiconductor fabrication process render the introduction of novel manufacturing techniques a challenge. In this talk, we present innovative concepts that have been developed and integrated within semiconductor fabrication tools. Emphasis is placed on point-of-use (POU) solutions and environmental engineering using plasma technologies. We review the requirements that must be met by green technologies to be integrated to a complex manufacturing environment. We also present arguments to demonstrate that environmentally benign manufacturing methods can be developed and implemented in an economically viable way.

2:40pm **IE-TuA3 Eliminating Perfluorocompound Gas Emissions from CVD Chamber Cleans*, P.J. Maroulis,*** *A.D. Johnson, W.R. Entley,* Air Products and Chemicals, Inc. **INVITED**

Perfluorocompond (PFC) gases such as CF4, C2F6, and NF3 are used extensively in semiconductor manufacturing processes. The largest volume use for these gases is for chamber cleaning following chemical vapor deposition (CVD). PFCs have long atmospheric lifetimes and absorb strongly in the infrared region of the electromagnetic spectrum where the earth's atmosphere would otherwise be transparent. Because of their infrared absorbances and persistence, PFCs are suspected of contributing to global warming. Through the World Semiconductor Council (WSC) the global semiconductor industry has voluntarily committed to reduce its cumulative emissions of perfluorocompounds. For the U.S., Europe, and Japan, PFC emissions will be reduced to 90% of 1995 levels by 2010 with some companies announcing even more aggressive reduction targets. Based on industry growth projections, substantial reductions for individual processes will be necessary to achieve these targeted levels. Both process optimization of traditional C2F6 based in situ cleans and substitution of NF3 for C2F6 in situ cleans are effective strategies for reducing the environmental impact of installed CVD tools. For new CVD tools, the manufacturers of semiconductor process equipment have developed and introduced a new remote NF3 cleaning technology that essentially eliminates PFC emissions. The combination of these three strategies, optimization of traditional C2F6 based in situ cleans, the substitution of NF3 for C2F6 in in situ cleans, and the implementation of the remote clean technology, has effectively solved the semiconductor industry's PFC issue. This presentation will contain data demonstrating the effectiveness of these strategies. In essentially all cases, perfluorocompounds emissions have been reduced by 50% to >99%.

3:20pm **IE-TuA5 Meeting IBM's PFC Emission Goals: Using the IBM In Situ Dilute NF@sub 3@/He Plasma Clean in Production on the Applied Materials 200 mm P5000 Lamp-Heated CVD Toolset*, C.M. Hines,*** IBM Microelectronics*; W.R. Entley, R.V. Pearce, A.D. Johnson,* Air Products and Chemicals, Inc.

The major use of perfluorocompounds (PFCs) in semiconductor manufacturing is for residue removal following thin film deposition in chemical vapor deposition (CVD) chambers. One promising strategy to reduce PFC emissions in CVD chambers is the use of alternative clean gases that have lower global warming potentials and inherently higher utilization efficiencies (the percentage of the PFC that is consumed during the clean process) than the traditionally used carbon based PFCs, CF@sub 4@ and C@sub 2@F@sub 6@. Using this strategy, IBM developed a one-step in situ dilute nitrogen trifluoride/helium (NF@sub 3@/He) clean to replace the process of record (POR) C@sub 2@F@sub 6@-based cleans used in their Applied Materials (AMAT) 200mm Precision 5000 lamp-heated (DxL) CVD chambers. Successful implementation of the dilute NF@sub 3@/He clean into production is considered key to IBM meeting its PFC reduction goals. Using quadrupole mass spectrometry (QMS) and Fourier transform infrared (FTIR) spectroscopy the process emissions of IBM's POR C@sub 2@F@sub 6@-based cleans and the new one-step dilute NF@sub 3@/He clean following deposition of both phosphosilicate glass (PSG) and tetraethylorthosilicate (TEOS) oxide were quantified. For TEOS oxide deposition the one-step dilute NF@sub 3@/He clean reduced the MMTCE value of the clean by 99 % with respect to the POR C@sub 2@F@sub 6@ clean. For PSG deposition, the one-step dilute NF@sub 3@/He clean reduced the MMTCE value of the POR clean by 96 %. In addition, the one-step dilute NF@sub 3@/He clean significantly reduced the total combined volumetric emissions of F@sub 2@ and HF compared to the POR C@sub 2@F@sub 6@ cleans. This presentation will include an overview of the implementation of the NF@sub 3@/He clean, current production data including tool performance (particles, mean time between wetstrips, etc.), and clean time/emissions comparisons between the POR C@sub 2@F@sub 6@ cleans and the one-step NF@sub 3@/He clean.

3:40pm **IE-TuA6 Treatment of Wastes from Chemical Mechanical Polishing Operations*, S. Raghavan,*** *Y. Sun, J. Baygents,* University of Arizona **INVITED**

Chemical mechanical planarization (CMP) of dielectrics and metals has emerged as one of the most important techniques used in the fabrication of integrated circuits. In this technique, dielectric and metal films are globally and locally planarized using particulate slurries made from submicron-sized alumina and silica particles. A multi platen CMP tool can typically process 40 wafers per hour at a slurry consumption of approximately 100 ml/min/wafer. The aforementioned tool, if integrated with a cleaner, will require two to three gallons per minute of DI water. The mixing of CMP waste with the post-CMP cleaning waste typically results in a waste stream that is a very dilute dispersion of solids containing approximately 500 to 5000 ppm solids. In the case of metal CMP, the waste is likely to contain metal ions, unreacted oxidant such as hydrogen peroxide, residual corrosion inhibitors and other additives that are present in the slurry. Wastes from copper CMP may contain anywhere between 10 and 40 ppm of dissolved copper, in the uncomplexed and complexed form. By the year 2002, chemical mechanical planarization processes are expected to account for thirty percent of water consumed in a fabrication facility. Because of this statistics, increasing pressure is put upon fabrication facilities to treat the CMP wastes and recycle the water. Additionally, environmental regulations at the local and national level demand that solids and copper ions be removed before disposal of the water to publicly owned treatment facilities. In this presentation, an overview of the CMP waste problem will be provided and various techniques available for the treatment of CMP wastes will be critically reviewed.

4:20pm **IE-TuA8 Advanced Chemicals for Semiconductor Processing*, E.R. Sparks,*** *W. Wojtczak, S.A. Fine,* ATMI **INVITED**

Three of the challenges to semiconductor processing are shrinking dimensions, copper metallization, and low-k dielectric materials. These challenges have been successfully addressed with a new group of water-based chemicals that fortuitously have very favorable properties. - As lithographic dimensions shrink, etching and other processing parameters become more stringent. The residues created from photoresist during these proceses often incorporate fluorocarbon residues, and silicon and metal oxides that are impossible to remove with traditional chemicals. - New processes using copper damascene metallization have additional constraints, as many traditional chemicals are not benign to copper. - Higher speed devices are attainable with low-k dielectric materials, but these materials have special chemical requirements. Advances have been made to meet all three of these requirements by formulating chemical mixtures that are more benign, both environmentally and regarding health issues, than previously possible. These blends are water-based, water-rinsable, and free of regulated solvents, i.e., "green". The resulting technology has a very favorable cost of ownership due to lower costs related to abatement and disposal, compared to more traditional solvent blends.

5:00pm **IE-TuA10 High Throughput Process for Photoresist Stripping and Residual Polymer Removal in a Via Post-Etch Process*, M. Boumerzoug,*** *Q. Geng, H. Xu,* Ulvac Technologies Inc.*; S. Gu,* LSI Logic Corporation*; S. Goh,* Silterra (M) Sdn. Bhd.*; T. Meyer, J. Seaton,* LSI Logic Corporation

In fabricating advanced IC, a multi-level interconnect scheme is commonly used and plasma etch is applied to form metal lines and via holes. During the plasma etch, a sidewall polymer is formed to control the etch profile. After the etch, the sidewall polymer needs to be removed completely to insure a good via contact resistance. Typically, a very aggressive amine based chemical solvent is needed to clean up the sidewall polymer. As the design rule shrinks and aggressive zero overplot of the metal line and via plug is used to minimize the die size, some degree of misalignment between via plug and metal lines is inevitable. Wet chemical based post etch cleaning starts to show problems for the misaligned via and metal because they may attack exposed Ti, W and Al. An advanced dry clean process has been developed for removing post etch polymer. In addition, the dry clean process offers a lower cost of ownership (COO) than the wet clean process and is much safer and environmentally friendly. This technology utilizes the combination of microwave downstream and non-damage ion assisted processes to strip chemically altered and damaged photoresist and clean residue according to the chemical composition of each layer. The ion-assisted process is also found useful in stripping the photoresist at high rate. After this dry process, no wet strippers are needed; thus, the high cost and environment and safety concern associated with chemicals can be eliminated. In some cases, this dry clean process becomes an enabling technology for avoiding Ti and W-plug attack occurring in the wet cleaning processes. Split lots of wafers, which have two layer metal, were processed by the all-dry processes and tested electrically. The via chain resistance, metal bridging yield, metal continuity and electrical CD are all equal or better than the control wafers which were processed by wet chemicals.

Incorporating Principles of Industrial Ecology
Room 304 - Session IE+PS+MS+SE-WeM

Environmentally Friendly Process Development
Moderator: D.R. Baer, Pacific Northwest National Laboratory

8:20am **IE+PS+MS+SE-WeM1 CVD Films as Directly Patternable Low-k Dielectrics***,* ***K.K. Gleason****,* *H.G. Pryce Lewis,* Massachusetts Institute of Technology*; G.L. Weibel, C.K. Ober,* Cornell University **INVITED**

As microelectronic feature sizes decrease to 100-nm and below, major advances in both interconnect and lithographic technologies are necessary. Novel low-k candidates being assessed include fluorine- and silicon-containing materials produced by chemical vapor deposition (CVD). Fluorine- and silicon-containing polymeric materials are also ideal resist candidates for 157-nm photolithography, as conventional photoresists are opaque at this wavelength. In this paper, we present a collaboration aimed at merging the role of sacrificial resist and low-k dielectric. Specifically, we are investigating a direct dielectric patterning process in which a low-k fluorocarbon or organosilicon material is deposited by CVD, exposed, and developed using no wet processing. In our scheme, a film is deposited using hot-filament CVD, a non-plasma technique which offers the ability to tailor film chemistries. The film is masked and exposed using e-beam or a 157-nm source, and developed using supercritical CO@sub 2@ as a dry developing medium. The patterned film then serves as a low-k material compatible with metallization schemes such as the damascene process. This technology would greatly simplify future device manufacture by reducing the number of steps involved in patterning. The CVD process and the use of dry development also offer environmental, safety and health advantages over solvent-based spin-on coating and aqueous development. Positive-tone contrast has been demonstrated in fluorocarbon CVD films and fully-developed images of 0.25-micron have been demonstrated from e-beam exposure. We are presently working to enhance sensitivity and optimize image resolution.

9:00am **IE+PS+MS+SE-WeM3 Characterization of Remote Plasma Clean Process for Plasma CVD Chamber***,* ***T. Tanaka****,* *T. Nowak, M. Seamons, B.H. Kim, K. Lai, M. Cox, P. Loewenhardt, D. Silvetti, S. Shamouilian,* Applied Materials Inc.

Remote plasma cleaning of CVD process chambers has proven to be more efficient than conventional in-situ plasma cleaning in terms of higher throughput and higher gas breakdown efficiency. It is still important, however, to maximize the efficiency of the remote plasma clean process because of the potential environmental impact and the cost of process gases. The remote clean process involves three steps: generation of reactive species (mostly fluorine atoms) in a remote plasma source, transport of the reactive gas, and the cleaning reaction in the CVD chamber. We studied the efficiency of the process in each step. Since accurate direct measurement of the atomic fluorine concentration in the various parts of the CVD reactor is difficult, we used etching of thermal oxide wafer coupons to estimate the relative distribution of atomic fluorine within the reactor. Source dissociation efficiency was studied using an indirect technique based on correlation of pressure to effluent composition. We found that it requires approximately 24eV to break down each NF@sub 3@ molecule. This translates to 1.7W/sccm of NF@sub 3@ flow. This was seen to be approximately the same for both a microwave discharge operating at 2.45GHz and an inductively coupled plasma at 13.56MHz. Results characterizing the transport step demonstrate the importance of system design on minimizing recombination losses of the reactive species which, for a parallel plate reactor, can be as high as 50% of the atomic fluorine generated in the remote plasma source. The experimental results are compared with a simple model, which describes the general behavior of the cleaning process.

9:20am **IE+PS+MS+SE-WeM4 Silicon Oxide Contact Hole Etching Process Employing Environmentally Harmonized Technique***,* ***K. Fujita****,* *M. Hori, T. Goto,* Nagoya University, Japan*; M. Ito,* Wakayama University, Japan

Etching process of SiO@sub 2@ contact holes in ULSI has been developed by using high-density plasmas employing stable PFC gases. PFC gases, however, cause a serious environmental problem, namely global warming and hereby the uses of fluorocarbon gases would be restricted in the near future. Recently, we proposed environmentally harmonized technique replacing stable PFC gases for preventing global warming, where polytetrafluoroethylene (PTFE) is evaporated by a CO@sub 2@ laser and the generated fluorocarbon species (C@sub x@F@sub y@) are injected into ECR plasma reactor from externally. This technique, therefore, enables us to achieve a novel plasma process with new gas chemistries. In this study, this system has been successfully applied to ECR plasma etching of SiO@sub 2@ contact hole and the behavior of CF@sub x@ (x=1-3) radical densities in the plasma were evaluated by infrared diode laser absorption spectroscopy (IRLAS). The high SiO@sub 2@ etching rate of 780 nm/min was obtained at a microwave power of 400 W, a pressure of 2.7 Pa, a total flow rate of 80 sccm and a bias voltage of -450 V. Dependence of contact hole etching characteristics on Ar dilution and pressure has been investigated. Anisotropy of contact hole etching was improved with increasing the Ar dilution ratio and decreasing the pressure because the fluorocarbon polymer deposition was suppressed at the higher Ar dilution and the lower pressure. IRLAS measurements indicate CF@sub 2@ radicals and higher radicals (C@sub x@F@sub y@) have the good relation with the polymer deposition. The anisotropic contact hole etching was achieved at an Ar dilution ratio of 90 %, a pressure of 0.4 Pa and the etching rate of SiO@sub 2@, selectivity of SiO@sub 2@ to Si and selectivity of SiO@sub 2@ to resist were 340 nm/min, 31 and 6.4, respectively. These results indicate that this environmentally harmonized technique will propose the alternative etching system replacing PFC gases.

9:40am **IE+PS+MS+SE-WeM5 Photocatalytic, Anti-fogging Mirror***,* ***K. Takagi****,* ULVAC Japan, Ltd., Japan*; H. Hiraiwa, T. Makimoto, T. Negishi,* ULVAC Japan, Ltd.

Recently, environmental pollution is growing more serious everyday, and it is urgently required to develop resource-saving and non-chemical products, which may save and even purify the nature. In such circumstances, titanium dioxide (TiO@sub 2@) thin coating film has come into the spotlight as a savior of the environmental problems. Because of its attractive photocatalytic natures, such as anti-bacterial, self-cleaning, decomposition of organic substances, and super-hydrophilic natures, TiO@sub 2@ has been studied and developed energetically in these days. Already, its super-hydrophilic and self-cleaning natures are applied to automobiles' anti-fogging side mirrors, which are now in practical use, and ULVAC Japan is one of the top makers for manufacturing vacuum deposition system for anti-fogging mirrors. The film architecture of this mirror is the double layer of SiO@sub 2@ / TiO@sub 2@ on the substrate coated by E/B evaporation or sputtering. The photocatalytic natures are as follows; 1. The contact angle of water on this surface is less than 10@Ao@ after irradiation of Blacklight, on which the engine oil is spreaded and cleaned by washing. 2. The contact angle keeps less than 10@Ao@ when this sample is preserved in the dark room. This report describes current developmental status of vacuum deposition system for TiO@sub 2@/SiO@sub 2@ thin film coating that is applied to automobile-mounted photocatalytic mirrors and is useful for environment saving and purification.

10:00am **IE+PS+MS+SE-WeM6 Low-k Materials Etching in Magnetic Neutral Loop Discharge Plasma***, Y. Morikawa, S. Yasunami,* ULVAC JAPAN Ltd.*; W. Chen,* ***T. Hayashi****,* ULVAC JAPAN Ltd., Japan*; H. Yamakawa, T. Uchida,* ULVAC JAPAN Ltd.

Many low-k materials, like Si containing inorganic / organic compounds, purely organic compounds and porous silicate glass, are proposed and examined as the interlayer dielectric one. The magnetic neutral loop discharge (NLD) plasma is very useful for very fine pattern etching process, because the NLD plasma has high density and low temperature characteristics and tends to form uniform density distribution on the substrate, at lower pressure region than 1 Pa under 13.56 MHz oscillating induction field.@footnote 1-3@ So we adopted the NLD plasma to etch organic low-k materials, with very high etch rate over 900 nm/min by using NH@sub 3@. An etching issue for the purely organic low-k materials is bowing in the hole smaller than 200nm in diameter, probably caused by reaction of the hole-wall surface with hydrogen atoms. Based on this consideration, we carried out the etching by using nitrogen gas mixed with a low concentration of hydrogen gas in low pressures below 1 Pa. The etch rate increased abruptly at hydrogen addition of a few quantity and approached gradually to a constant value at 20%. But the bowing size became larger above hydrogen mixed ratio of 20%. So we measured mass spectra of ion species produced in the plasma to know the mechanism. It was found that intensity of N2H+ also increased abruptly and then was close to a constant value at 20%. The other species did not show similar tendency. It is deduced from this result that N2H+ ion may participate in main etching reaction to obtain the conformal etched profile. Etching characteristics for OSG, pure organic low-k materials and porous silicate glass will be shown. @FootnoteText@@footnote 1@W.Chen, T.Hayashi, M.Itoh, Y.Morikawa, K.Sugita, H.Shindo and T.Uchida : Jpn. J. Appl. Phys., 38 (1999) 4296 @footnote 2@W.Chen, T.Hayashi, M.Itoh, Y.Morikawa, K.Sugita and T.Uchida : Vacuum, 53 (1999) 29 @footnote 3@W.Chen, T.Hayashi, M.Itoh, Y.Morikawa, K.Sugita, H.Shindo and T.Uchida : J. Vac. Sci. Technol. A17(5), (1999) 2546.

Incorporating Principles of Industrial Ecology
Room Exhibit Hall C & D - Session IE-WeP

Poster Session

IE-WeP1 Accurate Measurement for PFC by Mass Spectrometry using New Ionization*, M. Nakamura, K. Hino, T. Sasaki,* ***Y. Shiokawa,*** Anelva Corporation, Japan

To establish a method of accurate measurement for PFC is urgent global task. But, present methods by FT-IR and conventional mass spectrometry using electron impact ionization (EIMS) have serious problems: all kinds of by-products must be assumed before measurement and the quantitative results by the methods do not agree with each other. In order to overcome the problems, we have developed Ion Attachment Mass Spectrometry (IAMS) using new ionization@footnote 1@ and applied it to measurement of PFC. In IA MS, a Li@super +@ from heated Li-oxide emitter attaches moderately to a gas molecule. The excess energy caused by attachment is very small and is removed immediately owing to many collisions with other gases at 100Pa. Therefore, the gas with Li@super +@ a re not dissociated and becomes stable an ion as a whole. First, raw C @sub 4@F@sub 8@ without generating plasma was measured by IAMS. Quasi-molecule peak of C @sub 4@F@sub 8@Li appeared on the mass spectrum and any fragment peaks could not be found, whil e only fragment peaks appear by EIMS. Detectable limit of C @sub 4@F@sub 8@ was less than 1ppm. Other PFC gases such as C@sub 2@F@sub 6@, CHF@sub 3@ and SF@sub 6@ showed same results. Next, exhaust gases from dry etching system with generating plasma of A r, C @sub 4@F@sub 8@ and O@sub 2@ were directly introduced into IAMS and measured. Unreacted C @sub 4@F@sub 8@ and some expected by-products such as C@sub 2@F@sub 4@, CHF@sub 3@ were clearly confirmed from their quasi-molecule peaks. But, more than 10 kinds of unexpected by-products such as C@sub 2@H@sub 3@F@sub 3@, C@sub 3@H@sub 3@F@sub 5@, C@sub 4@OF@sub 8@ were detected, too. It seems likely that the existence of these unexpected by-products cause the disagreement between results by FT-IR and EIMS. @FootnoteText@ @footnote 1@ T.Fujii, Chemical Physics Letters 191 162 (1992).

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