Thursday Morning, October 28, 1999

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.

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

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