Monday Afternoon, November 2, 1998

Plasma Science and Technology Division
Room 314/315 - Session PS1-MoA

Environmental Issues and Emerging Technologies

Moderator: K.K. Gleason, Massachusetts Institute of Technology

2:00pm **PS1-MoA1 Scaling of PFC Abatement Using Plasma Burn-Boxes@footnote 1@**, ***X. Xu,*** *M.J. Kushner,* University of Illinois, Urbana-Champaign

Perfluorinated compounds (PFCs), gases which have large global warming potentials, are widely used in plasma processing for etching and chamber cleaning. Due to underutilization of the feedstock gases or by-product generation, the effluent from plasma tools typically have large mole fractions of PFCs. The use of plasma "burn-boxes" located downstream of the plasma chamber is being considered as a remediation method for abating PFCs emissions. In the burn-box, typically located between the turbo- and roughing pumps, O@sub 2@ is injected into a high density plasma with the goal of converting PFCs into products such as CO, CO@sub 2@, and COF@sub 2@. Results from the 2-dimensional Hybrid Plasma Equipment Model (HPEM) have been used to investigate the scaling of plasma abatement of PFCs using burn-boxes with ICP reactors. The HPEM is used to model the etching chamber of the ICP reactor to determine the utilization of the feedstock gases and generation of by-products. The effluent from the etching chamber is then passed through the burn-box using O@sub 2@ injection and excited by a second inductively coupled source. Results will be discussed for Ar/CF@sub 4@/C@sub 2@F@sub 6@/O@sub 2@ mixtures. We found that reassociation of PFCs after dissociation in the burnbox, particularly problemmatic for CF@sub 4@, is an important by-product generation mechanism which can be controlled to some extent by controlling the gas temperature. The abatement of C@sub 2@F@sub 6@ is approximately 4 times more efficient that CF@sub 4@ due to both the cited reassociation and and larger dissociation cross sections for C@sub 2@F@sub 6@. Full oxidation of the PFCs is possible, though large mole fractions of O@sub 2@, typically on order of 50%, are required. The radius of the burn-box, skin depth of the inductively coupled field and residence time of gases in the burnbox must be optimally selected in order to minimize "pass-through" of the effluent which reduces the abatement efficiency. @FootnoteText@ @footnote 1@Work supported by NSF and SRC.

2:20pm **PS1-MoA2 Point-of-Use Plasma Abatement of PFCs in a High Density Inductively Coupled Plasma**, *D.B. Graves,* ***E.J. Tonnis,*** University of California, Berkeley

A current major environmental concern in semiconductor manufacturing involves the use and emission of PFCs (perfluorinated compounds) and HFCs (hydrofluorinated compounds) during plasma etching of silicon dioxide and plasma-assisted chamber cleaning processes in dielectric film CVD systems.@footnote 1@ While significant progress has been made recently in reducing the emissions of PFCs and HFCs from CVD tools using alternate chemistries and process optimization, the stringent demands on oxide etch process recipes has limited emission reduction progress for etch. A promising alternate strategy for reducing or eliminating these emissions in etch processes is via point-of-use (POU) plasma abatement systems. In this approach, a high density plasma is ignited between the turbomolecular pump and the mechanical backing pumps downstream of a plasma process emitting HFCs and/or PFCs. A flow of O@sub 2@ is added upstream of the POU abatement plasma which dissociates the PFC/HFC and O@sub 2@ mixture causing the CF@sub x@ fragments to react with O atoms to form products that can be removed downstream through caustic water scrubbing processes. We present experimental results indicating that a high density, inductively coupled RF plasma can abate a variety of pure PFCs, including CF@sub 4@, C@sub 2@F@sub 6@, and CHF@sub 3@ in the presence of O@sub 2@ by between 90% and 99%. In addition, recent abatement experiments conducted on the effluent of an industrial high density oxide etcher indicate that these high levels of abatement can be realized even in the presence of complex mixtures of etch products found in actual tool exhausts. Issues that may limit POU plasma abatement implementation into an industrial environment such as process contamination, particulate formation, and transient control of the abatement plasma have also been examined. @FootnoteText@ @footnote 1@The National Technology Roadmap for Semiconductors, Semiconductor Industry Association, pp. 154-157, 1997.

2:40pm **PS1-MoA3 Plasma Etching Using PFC Replacement Chemicals**, *T. Kure,* Hitachi Ltd., Japan; *T. Takaichi,* Showa Denko K.k., Japan; ***Y. Goto,*** Hitachi Ltd., Japan **INVITED**

PFC (Perfluorocompound) gases are widely used for plasma etching of thin film and for plasma cleaning of process chamber. However, unfortunately, PFCs have extremely long atmospheric lifetimes and absorb infrared radiation emitted by the earth that would otherwise be radiated into space. As a result, PFCs contribute to the greenhouse effect in the earth's atmosphere, thus helping to cause the phenomenon known as a global warming. To reduce the release of PFCs into the air, replacement chemicals and abatement devices for exhaust gases need to be developed. Recently, several kind s of abatement devices (combustion, plasma, thermal, and catalyst reaction) are being examined. In our research, we have focused on using iodofluorocarbons (IFCs) and unsaturated fluorocarbons (u-FCs) as replacement chemicals for PFCs. Since the binding energy of C-I bond and C=C bond are very weak compared with the C-F bond, the atmospheric lifetimes of IFCs and u-FCs are extremely short. Therefore, their impact on global warming should be small. For use in SiO@sub 2@ etching, we selected C@sub 2@F@sub 5@I and C@sub 3@F@sub 6@ because of its C/F ratio about 0.5, its boiling point less than room temperature, and nonflammability. We evaluated the SiO@sub 2@ and poly-Si etching rate in a microwave plasma with these gases comparing it with C@sub 4@ F@sub 8@ gas. We also evaluated XPS spectrum of deposited polymer on etched wafers. We found that both the etching performance and deposited material were similar among these gases. Therefore, we believe C@sub 2@F@sub 5@I and C@sub 3@F@sub 6@ can be used as replacement chemicals for PFCs in SiO@sub 2@ etching.

3:20pm **PS1-MoA5 Challenges in Plasma Etching and Patterning for Fabrication of New Systems and Devices**, ***M. Engelhardt,*** Siemens AG, Germany **INVITED**

Among the most challenging tasks of plasma process technology today are, without doubt, plasma etching for fabrication of through-wafer interconnects in wafer stacks for vertical integration of chips (VIC) and plasma patterning of new materials used for electrodes and storage media in storage capacitors of Gbit scale DRAMs and FeRAMs. VIC realized by stacking and vertically interconnecting fully processed device wafers allows fabrication of both new systems with unique system qualities and systems with highly improved performance. 3D integration approaches are also driven by the interconnect crisis. Through wafer interconnects used for 3D chip integration require plasma etching of dielectrics, single cristal silicon, and interchip glue layers at aspect ratios exceeding 15 for vias through wafers thinned down to 15µm. Vertical profiles achieved with minimized RIE lags and high etch rates are the stringent requirements for all of these processes. Patterning of Pt electrodes is another challenging task. So far no volatile reaction products were obtained at usual process temperatures. Processes based on so-called reactive gases leading to a build-up of transient or removable sidewall films result in significant sidewall taper of the profiles and hence high CD gain whereas steep profile sidewalls have been obtained with processes based on inert gases with the tradeoff of build up of non-removable sidewall films. A new approach overcomes these tradeoffs by a combination of plasma patterning and CMP allowing fabrication of vertical Pt profiles with resist mask. The build-up of thin redepositions of Pt onto the sidewalls of the resist, obtained as a result of processing in pure Ar plasmas, is utilized to achieve a sidewall steepness of the patterned Pt film which is determined by the steepness of the pre-etch resist profile. After pattern transfer and resist stripping, the portion of the redepositions protruding above the fabricated storage node was completely removed by CMP.

4:00pm **PS1-MoA7 PECVD and Dry Etching on Large Glass Substrates for Flat Panel Displays**, ***J.M. Perrin,*** Balzers Process Systems, France **INVITED**

Flat panel display manufacturing depends more and more on plasma processing. This is particularly the case in the fabrication of the thin film transistor (TFT) array for active matrix liquid crystal displays (AMLCD's). Besides PVD of metals or metallic compound films by magnetron sputtering, and PECVD of amorphous silicon (aSi) and silicon nitride or oxide, plasma dry etching is gradually taking over wet etching, still abundantly used in first and second generation fabrication lines. We will focus on process issues, reactor concepts, and architectures of processing tools for PECVD and plasma dry etching, both performed in RF-excited glow discharges. The evolution of process demand in PECVD goes towards i) a better control of film and interface quality to achieve thinner TFT's and improved aSi TFT mobilities, ii) the deposition of aSi films suitable for laser crystallization to produce polycrystalline Si TFT's, and iii) the deposition

silicon oxide instead of nitride as gate insulator. For dry etching the general trends are i) the development of dry-etching of metal source and drain contacts which is very critical in the back-channel etch TFT technology, ii) the reduction of the number of masks trend by etching multilayers of metals, and iii) etching of the ITO pixels. The increasing size of glass substrates to (up to 1 m2) imposes severe constraints on the design of reactors, to insure process uniformity, deposited film quality, and control of etch profiles. The most widely used concept still remains the classical capacitively-coupled RF discharge configuration. But the scaling up of such sources involve problems such as the uniformity of RF power distribution and gas feed on the electrodes. Moreoverreactive ion etching faces the problem that the RF discharge become more and more symmetric as the ratio of RF-powered electrode and grounded electrode areas tends towards unity. To overcome this problem of scaling-up, and provide control of the ion energy on the substrate, we have developed a new triode configuration (Piano reactor) involving a periodic structure of isolated bars with independent RF impedances to ground. Then comes the production issue related to the best way to achieve a large throughput. The debate is between the development of high rate plasma sources or processes with fast substrate handling in a cluster type configuration, or keeping moderate deposition and etch rate in stacks of reactor with parallel processing. Eventually reactor maintenance issues such as dry-cleaning after PECVD are critical.

4:40pm **PS1-MoA9 Use of a One Atmosphere Uniform Glow Discharge Plasma (OAUGDP) to Kill a Broad Spectrum of Microorganisms@footnote 1@**, ***K. Kelly-Wintenberg***, *A. Hodge, T.C. Montie, L. Deleanu, J.R. Roth, D. Sherman,* University of Tennessee*; P. Tsai, L. Wadsworth,* Textile and Nonwovens Development Center (TANDEC)

The medical, industrial, and food processing industries are constantly in search of new technologies to improve existing sterilization and pasteurization methodologies. Available techniques must deal with and overcome such problems as thermal sensisitivity and destruction by heat, formation of toxic byproducts, cost, and inefficiency in performance. We report the results of a newly invented plasma source, a One Atmosphere Uniform Glow Discharge Plasma (OAUGDP) that is capable of operating at atmospheric pressure in air and providing antimicrobial active species at room temperature. OAUGDP exposures have reduced log numbers of bacteria (E. coli, S. aureus, Deinococcus radiodurans, and Bacillus subtilis), bacterial endospores (Bacillus subtilis and Bacillus pumilus), and various yeast and bacterial viruses on a variety of surfaces. These surfaces included polypropylene, filter paper, paper strips, solid culture media, and glass. Experimental results showed at least a @>=@ 5 log@sub 10@ CFU reduction in bacteria within a range of 15-90 sec of exposure, whether the samples were exposed in conventional sterilization bags or directly exposed to the plasma. An exception to these very short exposure times were experiments with solid culture media where 5 min of plasma exposure was necessary to produce @>=@ 5 log@sub 10@ CFU reduction in bacterial counts. The effects of plasma treatment on bacterial cell structures were investigated by exposing cells to plasma for various durations and examining them by Transmission Electron Microscopy. These experiments showed cell lysis had occurred with the release of cellular contents. These data were consistent with spectrophotometer data in which the release of cellular constituents was measured as a change in absorption at 210nm and 260nm. With all microorganisms tested, a bi-phasic killing curve (logarithmic number of survivors versus time) was generated in plots of doseresponse data. Differences in susceptibilities of microorganisms observed on various surfaces suggested that the degree of lethality was dependent upon the time of diffusion of active species and the makeup of the microbial cellular surface. @FootnoteText@ @footnote 1@This work was supported in part by the Air Force under a STTR with Environmental Elements, Inc. of Baltimore, MD; and by the UTK Textiles and Nonwovens Development Center (TANDEC).

5:00pm **PS1-MoA10 High Pressure Plasmas as an Anti-Terrorist Technology**, ***G.S. Selwyn***, *H.W. Herrmann, I. Henins,* Los Alamos National Laboratory

Plasmas have long been used for production of short-lived, reactive chemical species needed for etching or deposition of thin films. Plasmas are also widely used for dry ashing or stripping of organic films, such as photoresist, from wafers. We have recently developed a novel, atmospheric pressure, non-thermal plasma source with chemical and electrical characteristics closely resembling traditional low-pressure plasma discharges. However, unlike conventional low pressure plasmas, this source produces a fast-flow stream of chemically-reactive, metastable species capable of selective surface oxidation. One emerging application for this new technology is the use of plasmas for decontamination of civilian and/or military targets attacked by chemical or biological warfare agents. We have demonstrated rapid and effective decontamination of surfaces exposed to either anthrax-surrogate spores or a chemical agent used as a surrogate for mustard gas. Anthrax is an air-borne, persistent and highly toxic spore capable of causing mass casualties if spread in an urban area by terrorist. The atmospheric pressure plasma jet (APPJ) has been shown to produce a 7-log decrease in active spores after a 90 second exposure to the reactive effluent stream. Mustard gas is a chemical agent causing severe skin blistering, mass injuries and incapacitation capable of lasting several months. It can be used to reduce the effectiveness of military force and to interfere with military logistics as well as to render urban areas uninhabitable for prolonged periods. The APPJ source has been shown to detoxify a mustard gas simulant by 5 orders of magnitude in just 30 seconds of effluent exposure. Development of this new technology provides a potential means of defeating terrorist attacks using these agents, both in the US and overseas. By providing a means to effectively counter chemical and/or biological attacks, it is hoped the use of these weapons of mass destruction will also be deterred.

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