Plasma Science and Technology Division
Room On Demand - Session PS-Invited On Demand
Plasma Science and Technology Invited On Demand Session

PS-Invited On Demand-1 Control of Interface Layers for Selective Atomic Layer Etching, ***Takayoshi Tsutsumi,*** Nagoya University, Japan*; R. Vervuurt,* ASM, Japan*; N. Kobayashi, M. Hori,* Nagoya University, Japan **INVITED**

Atomic layer etching (ALE) processes with material selectivity are expected to be key to fabricate nano-sheet transistors, nanowire transistors and other three-dimensional devices. We have developed a plasma-enhanced ALE process using an energetic ion to form a self-limiting interface layer denoted by a modification or a mixture layer, which is sequentially removed by the plasma. This presentation focuses on the reaction mechanisms to achieve selective ALE processesfor silicon-compoundsby controlling the interface layer.

First discussed is the mixture layer formed by fluorocarbon plasma during the ALE of silicon oxide. We developed an atomic scale etching using alternating nanometer-thick fluorocarbon film deposition and O_2 plasma irradiation for silicon oxide.[1] The Ar ion enhances the reaction at the interface between the silicon oxide and fluorocarbon and forms a mixture layer which consists of carbon, fluorine, silicon and oxygen.. Therefore, control of the fluorocarbon film thickness and composition are required to improve repeatability of etched thickness per cycle and material selectivity in the process. The process achieved high process repeatability against cycle numbers because the O_2 plasma maintained a stable surface of the SiO_2, and removed excess carbon atoms as gaseous products such as CO. The O_2 plasma also initializes the chamber conditions in each cycle. We investigated the depth profiles of atomic concentrations in the mixture layer to improve the material selectivity.

Second discussed is the modification layer formed and by H_2 plasma and its removal step by fluorinated plasma.[2] We investigated the surface modification and etching mechanism by *in-situ* spectroscopic ellipsometry and attenuated total reflectance Fourier transform infrared (FTIR) spectroscopy.[3] The in-situ analysis clarified that the hydrogen plasma induced an increase in the concentration of Si−H and N−H bonds, and the N−H bond concentration plateaued more quickly than Si-H bonds. Considering the temporal change in the concentration of Si−H and N−H bonds during removal step by fluorine radical, Si−H bonds were primarily present near the surface, while N−H bonds were mainly located deeper into the silicon nitride film.

Based on the results, we will show understanding of the reaction mechanism helps to improve the controllability and the selectivity in ALE.

[1]T. Tsutsumi et al., J. Vac. Sci. Technol. A **35**, 01A103 (2017).

[2]S. Sherpa et al., J. Vac. Sci. Technol. A **35**, 01A102 (2017).

[3]K. Nakane et al., ACS Appl. Mater. Interfaces **11**, 37263 (2019).

PS-Invited On Demand-7 Current Modeling and Simulation Challenges of Low-Temperature Plasmas, ***Anne Bourdon,*** LPP, CNRS, Ecole Polytechnique, France **INVITED**

Low-temperature plasmas are used for applications ranging from material processing to bio-medical and electric propulsion applications. To model these discharges many physical and chemical processes have to be considered as multi-species nonequilibrium gas chemistry and transport, coupling of charged species with electromagnetic fields, coupling of the discharge with the fluid dynamics of the reactive gas, and coupling with surfaces and interfaces. For the modeling and simulation of these discharges, a major challenge is related to the very different space and time scales these processes may have. In the last decade, advances have been obtained on the mathematical modeling and high performance computing of low-temperature plasmas. In particular, the possibility to use multi-scale coupling methods, structured, unstructured, and adaptive mesh techniques, new algebraic equation solvers and parallel computing have opened a large range of new simulation possibilities. To illustrate some recent developments and current challenges in the field of modeling and simulation of low-temperature plasma discharges, two examples will be presented: fluid simulations of atmospheric pressure plasma jets for biomedical applications and plasma assisted combustion and PIC and fluid simulations of low-pressure magnetized plasmas for electric propulsion.

PS-Invited On Demand-13 Plasma-Substrate Interaction in the Case of Atmospheric Pressure Plasmas, ***Ana Sobota,*** Eindhoven University of Technology, Netherlands*; O. van Rooij,* Eindhoven University of Technology, Afghanistan*; M. Hofmans, O. Guaitella, A. Bourdon,* Ecole Polytechnique, Afghanistan*; P. Viegas,* Dutch Institute for Fundamental Energy Research (DIFFER), Afghanistan **INVITED**

Non-thermal plasmas are a versatile tool for applications at atmospheric pressure and in interaction with various substrates, but it has also been established that the substrates modify the plasma during the interaction. This work examines the effect on electron and heavy particle properties and discharge development.

PS-Invited On Demand-19 Recent Advances in Plasma Processing for the Creation of Tunable Biofunctional Surfaces and Interfaces, ***Marcela Bilek****, B. Akhavan, C. Tran, R. Walia, E. Kosobrodova,* University of Sydney, Australia*; A. Kondyurin,* university of Sydney, Australia*; C. Lotz, G. Yeo,* University of Sydney, Australia **INVITED**

Bio-functionalized surfaces are of great interest for a wide range of applications, particularly in biomedical diagnostics and implantable medical devices. We have shown that radicals embedded in carbon-rich surfaces facilitate simple, one-step surface-functionalisation [1]. The radicals are created by energetic ion bombardment of the surfaces. Reagent-free, covalent immobilisation of functional molecules occurs on physical contact by immersion or spotting / painting of the biomolecule-containing solutions onto the activated surfaces. This strategy simplifies covalent functionalisation of surfaces enormously and the approach can immobilise bioactive peptides, antibodies, enzymes, single stranded DNA, and extra-cellular matrix proteins [2] onto many materials, including polymers, metals and ceramics. Applications enabling biological studies of the response of individual cells to proteins on a sub-cellular scale [3], and the preparation of multi-functionalisable nanoparticles for theranostics [4] have been demonstrated. Spontaneous covalent immobilisation coupled with tuning of electric fields in double layers at the surface during the immobilization, created by pH variations and/or the application of external electric fields, enable control of the density and orientation of surface-immobilised bioactive peptides [5].

This presentation will review the underpinning science and report recent advances that extend the application of these techniques to functionalisation of the internal surfaces of complex, porous materials and structures using controlled flow fields and strategically designed electrodes to create plasma discharges within the internal spaces. The efficacy of embedded radicals to polymerise and covalently link hydrogels to solid surfaces and the use of atmospheric pressure plasma discharges to activate surfaces for covalent biofunctionalization during 3D bioprinting will also be explored.

[1] *PNAS* **108**:14405-14410 (2011); [2] *Appl. Surf Sci***310**:3-10 (2014); [3] *ACS Appl. Mater. and Interfaces* (2018); [4] *ACS Appl. Nano Materials* (2018); [5] *Nat. Comm.* 9:357(2018)

PS-Invited On Demand-31 Linear Hollow Cathode Plasma Source and the Deposition of Silicon Oxide Materials, ***John Chambers,*** AGC*; E. Michel, G. Arnoult,* AGC, Belgium **INVITED**

AGC's proprietary Linear Hollow Cathode electrodes are used to generate uniform linear plasma for PECVD.The patented technology drives pairs of electrodes using typical mid-frequency or pulsed-DC power supplies that are designed for magnetron sputtering.The linear hollow cathode technology uses electrode geometry to confine electrons and generate a dense plasma, and therefore does not require any magnetic field to maintain a linear discharge.

This novel plasma generation method allows for stable plasma discharge under a variety of process conditions -- notably under a wide range of process pressures.Since magnetic field is not necessary for plasma generation, other magnetic fields may be used to shape the plasma within the process chamber.

Additionally, the PECVD process allows for variation of plasma gas and precursor materials, as well as extreme variation in their flow rates and ratios.The combination of these process flexibilities allows for the deposition of materials with varied properties, such as silicon oxide materials of variable density and refractive index.

AGC Plasma Technology Solutions develops this technology for AGC's own internal production processes, as well as for marketing outside of their glass coating industry for use in plate-to-plate and roll-to-roll coaters.

John R. Chambers*

John.Chambers@us.agc.com

415-684-8438

AGC Plasma Technology Solutions

Sacramento R&D Facility

9881 Horn Road, Suite F

Sacramento, CA 95827

Eric Michel, PhD

Eric.Michel@eu.agc.com

AGC Glass Europe S.A - Coatings Department

AGC Technovation Centre

Rue Louis Blériot, 12 | B-6041 Gosselies Belgium

Grégory Arnoult, PhD

Gregory.Arnoult@eu.agc.com

AGC Glass Europe S.A - Surfaces Department

AGC Technovation Centre

Rue Louis Blériot, 12 | B-6041 Gosselies Belgium

PS-Invited On Demand-37 CO_2 Conversion in Microwave Plasma: Can We Bring It to an Industrial Scale?*, **Floran Peeters**,* Dutch Institute for Fundamental Energy Research, Netherlands **INVITED**

With increasing global interest in renewable energy technology, storage of electrical energy has become particularly relevant. The chemical industry must likewise be transformed to rely only on sustainably generated electricity to convert common molecules such as N_2 and CO_2 into chemical building blocks or fuels. Plasma-driven conversion has great potential for upscaling, since no rare materials are required in construction or upkeep, while also being compatible with the intermittent nature of sustainable electricity sources. Using plasma powered by microwaves, high power densities, and thus high throughputs, can be obtained. Moreover, since the plasma is essentially electrode-less, degradation of the reactor over time is virtually non-existent.

This contribution provides an overview of lab-scale results obtained from microwave plasma reactors. With a focus on CO_2 as the main input gas, a full description of the conversion process in these reactors will be given, pieced together from gas composition and temperature diagnostics, combined with both gas flow and chemical kinetic modeling. The importance of transport of both species and heat to and from the plasma will be highlighted.

Using the insights gained from these experiments and models, strategies for further improvement of the conversion process will be sketched. Included in this analysis are the potential for heat recycling and heat integration to improve energy efficiency in the plasma, the energy costs involved in peripheral processing steps such as expansion or compression of the feedstock gas, and the possibilities for integrating the separation of product species such as O_2 and CO from the output gas stream. A rough cost calculation will be used to assess to what extent plasma might be used to turn CO_2 into a chemical building block.

PS-Invited On Demand-43 2021 AVS PSTD Young Investigator Award Talk: Plasma Treatment on SiGe for Improvement of Interface Trap Density by Inducing Si Segregation*, **Yohei Ishii**[1],* Hitachi High-Tech America, Inc.*; R. Sugano,* Hitachi, Ltd., Japan*; Y. Lee, W. Wu,* Taiwan Semiconductor Research Institute, Taiwan*; H. Ishimura,* Hitachi High-Tech Taiwan Corp., Taiwan*; K. Maeda, M. Miura,* Hitachi High-Tech Corp., Japan **INVITED**

Transistor structure was modified from planar into Fin-type Field Effect transistor (FinFET), in order to improve short-channel effects due to the device scaling. Although FinFET has been widely applied recently, further scaling is still required to follow Moore's law. However, the continuous scaling is getting more challenging due to the reality approaching toward atomistic-level control of pattern pitch. One of the methods to enhance electrical performance in FinFETs is the use of silicon (Si) in n-FETs and silicon germanium (SiGe) in p-FETs due to the higher hole mobility [1]. This is one of the promising candidates for sub-10nm process.

In order to enhance SiGe characteristics in addition to the use of SiGe, reducing interface trap density is critical for sub-threshold improvement [2]. This can be achieved to produce Si-rich surface at SiGe/gate-oxide interface on SiGe surface, because unstable GeO_x leads to charge trap defects at the interface [3]. There are two processes used conventionally to realize the Si-rich surface: atomic layer deposition of Si cap over SiGe fin [4] and GeOx scavenging process [3]. However, these methods require the use of high temperature, which may bring about strain relaxation in the SiGe channel and Ge diffusion into Si substrate. To avoid the deterioration of the SiGe characteristics, low temperature process is desirable. However, the SiGe composition control at low temperature process has not been studied yet.

In this study, we developed low-temperature plasma treatment that induces Si-rich modification layer on SiGe surface. We revealed that the mechanism to realize the Si-rich surface is caused by Si segregation behavior under the plasma treatment experimentally. We will also present that the surface composition modulation was energetically favorable using ab-initio calculation. The details of the plasma treatment is further discussed experimentally, in conjunction with ab-initio calculation.

[1]. O. Weber et. al., IEDM Tech. Dig., p.719, 2007

[2]. C. H. Lee et. al., IEDM Tech. Dig., p.31.1.1., 2016

[3]. C.H. Lee, et. al., VLSI Tech. Dig., p. 36, 2016

[4]. H. Mertens, et al., VLSI Tech. Dig., p.58, 2014

PS-Invited On Demand-55 Going Mobile: Design, Optimization, and Scaleup of Plasma Reactors for Treatment of Pfas-Containing Ion Exchange Brine*, **Selma Mededovic Thagard**,* Clarkson University **INVITED**

Poly- and perfluoroalkyl substances (PFAS) have recently received considerable attention due to their toxicity, ubiquitous presence and recalcitrance in the environment. Current large-scale treatment of groundwater contaminated with PFAS involves using an ion exchange (IX) resin. In regenerable IX systems, the regeneration of the resin yields still bottoms or brine, a complex and highly electrically conductive chemical mixture of high concentration PFAS, methanol (usually recovered by distillation), and sodium chloride that is expensive to dispose of and often must be stored on-site. A promising solution to the disposal of brine is through plasma-based water treatment, a low-cost, low energy process which has been demonstrated to be extremely efficient in degrading a range of PFAS.

In this work, we have adapted a proven plasma-based treatment system for low concentration, low conductivity PFAS-contaminated water so that it can treat regenerant brine. A bench-scale point-point discharge reactor was developed to investigate the influence of solution electrical conductivity and ion composition on the performance of the reactor in treating a single PFAS-perfluorooctanoic acid (PFOA)-in a solution containing sodium chloride that was used to adjust the solution conductivity between 0.3 and 45 mS/cm.The influence of various ions was explored using chlorine and non-chlorine salts to adjust the conductivity.

Following bench-scale investigations, the reactor was upscaled for the treatment of large volumes of brine. A "high-concentration" and a "low-concentration" bench-scale batch plasma reactors were developed and used successfully to degrade PFAS at high concentration (>100 mg/L) and low concentration (< 1 µg/L), respectively, in still bottom solutions containing numerous PFAS with a wide concentration range. The reactors were installed into a mobile trailer and demonstrated in the field earlier this year at an Air Force Base.

PS-Invited On Demand-61 Plasma Process Requirements for Emerging Memories*, **Nicole Saulnier**, I. Saraf, A. Dutta, K. Brew, S. Mehta, P. Jamison, O. van der Straten, I. Ok, S. Seo, C. Silvestre, C. Yang, M. Rizzolo, S. Choi, H. Chen,* IBM Research Division, Albany, NY*; P. Adusumilli,* IBM Research Division, T.J. Watson Research Center*; J. Arnold,* IBM Research Division, Albany, NY*; D. Edelstein,* IBM Research Division, T.J. Watson Research Center*; J. Slaughter,* IBM Research Division, Albany, NY*; T. Ando,* IBM Research Division, T.J. Watson Research Center*; A. Sebastian,* IBM Research GmbH, Zurich Research Laboratory **INVITED**

The industry is experiencing a surge of interest in new memories, and their integration with logic devices. Some of this interest is driven by the slowdown in traditional device scaling, which is creating opportunity for fast, dense, low power memory that can be closely coupled to processors without consuming precious silicon area. Another very powerful driver of interest in non-traditional memories is Analog Artificial Intelligence (AI), where there is tremendous potential for speed and energy efficiency improvements by using arrays of non-volatile multi-state memory elements to store the weights linking nodes within neural networks.

Both applications for emerging memories have a distinct set of device metrics which must be met to achieve the desired technology performance. These device metrics can be sensitive to the applied

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processes and introduce new requirements for the plasma processes used to deposit materials, pattern structures, treat surfaces, etc. For the analog AI application space, devices should have low stochasticity and low variability across a range of states. A population of devices should be able to be programmed into each desired state and should remain in that state until it is intentionally updated. Both phase change material (PCM) devices and Resistive RAM (RRAM) devices are susceptible to plasma processes during device integration. For a more traditional memory application, device metrics are relaxed since the device needs to achieve only two states. These states are typically far enough apart that concern of overlap is low. However, these devices need to be densely packed so they tend to have smaller CD and pitch compared to devices being considered for analog AI applications. One example of an emerging memory that is considered as an SRAM or DRAM replacement is Magnetoresistive RAM (MRAM). The small geometry and complex materials stack used for MRAM devices can be a challenge for integration and patterning. In addition to these applications introducing new requirements, many of these memory devices involve the introduction of materials not typically used in semiconductor devices. Emerging memories which introduce new sensitivities and/or new materials will drive a need for new processes, chemistries, and tools to achieve efficient, high yield, and scalable fabrication.

This paper will present a handful of case studies, each of which examines an emerging memory device. The new device's requirements will be reviewed, along with the current common practices for fabrication. Discussion of the limitations of those current processes will highlight opportunities for further research and development.

This work was performed by the Research Alliance Teams at various IBM Research and Development Facilities

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