Plasma Science and Technology Division
Room 315 - Session PS2+SE-FrM

Plasma Sources, Diagnostics, Sensors and Control
Moderator: Nathan Marchack, IBM T.J. Watson Research Center

8:20am **PS2+SE-FrM-1 Optical and Electrical Diagnostics of Industrial Plasma Reactors: Measuring the Relevant Physical Quantities to Assist Process Development***, **Gilles Cunge**,* LTM/CNRS-UJF, France*; S. Younesni,* STMicroelectronics/CNRS-LTM France*; N. Loubet, M. Kogelschatz, E. Pargon, C. Petit-Etienne, O. Joubert, E. Despiau-Pujo, N. Sadeghi,* CNRS-LTM, Université Grenoble Alpes, France **INVITED**

As new devices with 3D architectures and new materials are introduced in the microelectronic industry, plasma etching processes are more and more challenged. The necessity to pattern nanometer size features (with high aspect ratio) with an ultrahigh selectivity towards underlayers has pushed the development of new plasma processes with advanced RF power and/or gas injection pulsing schemes. The goal is either to achieve atomic layer etching processes or simply to overcome typical plasma limitations (charging effects, ARDE…etc). However, since the number of different processes possible in a reactor increases rapidly with each new control knob, the development of innovative processes is becoming extremely difficult with empirical approaches (i.e. DOE). It is thus mandatory to get a deep understanding of the impact of knew control knobs on the plasma properties to develop such new processes efficiently, which can only be achieved by using plasma and surface diagnostics. In this paper, we will review plasma diagnostics that are the best adapted to get a clear picture of the impact of the reactor control knobs on the process performances. Plasma diagnostics are separated in two categories: 1) those used to detect radicals (etchants or etch products) with a time resolution of about 1 ms, i.e. modulated beam mass spectrometry as well as spectroscopic techniques such as optical emission spectroscopy, absorption spectroscopy (from the VUV to near IR range) and Laser induced fluorescence. 2) techniques used to measure the charged species with a µs time resolution: specific Langmuir probe for the ion flux measurements in aggressive environment, RFEA for ion energy distribution function and mass spectrometry/RFEA to analyses the ion nature. We will show that it is important to couple plasma diagnostics with surface analysis (e.g. XPS, Raman…etc) to get a clear picture of the mechanisms involved in new processes and illustrate this point with several concrete processes developments in industrial reactors (ranging from pulsed ICP plasmas to downstream processes).

9:00am **PS2+SE-FrM-3 Hole Transport Properties of Nickel Oxide Films Grown via Hollow-Cathode Plasma-Assisted Atomic Layer Deposition***, S. Ilhom, A. Mohammad, M. Niemiec, D. Zacharzewski, P. Chardavoyne, S. Abdari, **Necmi Biyikli,*** University of Connecticut

In contrast to the relative abundance of as-grown unintentionally doped n-type semiconductor materials, there are only a few alternative alloys showing p-type conduction without needing extra high-temperature doping processes. NiO is of particular interest mainly due to its stability and promising performance as hole-transport layers in emerging solar cell device structures. However, to broaden the NiO application domain towards potential back-end-of-the-line (BEOL) transistor devices as potential p-type channel layers, the transport properties of NiO needs to be improved significantly. While low-temperature thermal, plasma, and ozone-assisted ALD efforts have resulted in p-type NiO films with atomic-level precision and large-area uniformity, the hole mobility is far from being sufficient, typically lower than 1 cm^2/Vs.

In this study we have carried out a systematic study on plasma-enhanced ALD (PEALD) of NiO films on Si and glass substrates using nickelocene ($NiCp_2$) and O_2/Ar plasma mixture using hollow-cathode plasma-assisted atomic layer deposition (HCP-ALD). Detailed saturation studies using in-situ ellipsometer monitoring were carried out in the HCP-ALD reactor, scanning for $NiCp_2$ pulse time, O_2 plasma exposure time, purge time, and plasma power. Optimal growth conditions were identified as 90 ms $NiCp_2$ pulse / 5 s purge / 10 s O_2-plasma at 100 W plasma exposure / 5 s purge. 800 cycle runs were conducted to evaluate the substrate temperature impact (100 - 250 °C) on growth-per-cycle (GPC) and film properties.

The resulting p-type NiO films are characterized for their structural, optical, and electrical properties. Films grown at optimal conditions (200 °C) exhibit refractive index values reaching 2.3, which is in good agreement with reported values for the best polycrystalline NiO films in the literature. NiO films deposited on both Si and glass substrates exhibit polycrystalline single-phase cubic structure (*c*-NiO). In order to determine the carrier type and extract field-effect mobility values, we have fabricated vertical NiO/n-Si p-n junction diodes as well as NiO/Al_2O_3/Si thin-film-transistor (TFT) device prototypes to characterize diode I-V behavior and confirm p-type layer structure for NiO, and extract the field-effect carrier mobility, respectively. Our I-V measurement results confirmed p-n junction diode characteristics with decent ON/OFF ratios for forward and reverse diode current values. TFT characterization results as well as detailed temperature-dependent Hall measurements will be used to identify critical hole transport parameters.

9:20am **PS2+SE-FrM-4 In-Situ Measurement of Electron Emission Yield at Silicon Surfaces in Ar/CF4 Plasmas***, **Mark Sobolewski,*** NIST

Plasma simulations require accurate data for the ion-induced electron emission yield at plasma-exposed surfaces. For industrially relevant plasmas, however, direct measurement of yields using ion beams is impractical. In contrast, measurements made in situ, during plasma exposure, provide useful values for the total or effective yield produced by all incident ions. Here, in-situ measurements were performed in an icp system in Ar/CF4 mixtures at 1.3 Pa. The current and voltage across the sheath adjacent to the rf-biased substrate electrode were measured, along with Langmuir probe measurements of ion current density and electron temperature. The measurements are input into a numerical sheath model, which allows the emitted electron current to be distinguished from other currents. The effective yield was determined for thermally oxidized, in-situ etched, and sputter-cleaned silicon surfaces. For thermal oxides in pure Ar, yields agreed with previous measurements [1] on sputtered oxides. By combining measurements made for several mixtures with mass spectrometer data for the relative flux of each ionic species, estimates or bounds were obtained for the individual electron emission yields of the most prevalent ions. [1] M. A. Sobolewski, Plasma Sources Sci. Technol. 30 025004 (2021).

9:40am **PS2+SE-FrM-5 Plasma Characterization: Radical Recombination Sensor Based on Dual Probe Thermopile Heat Flux Sensors***, **Johannes Velthuis,*** TNO Science and Industry, the Netherlands

Hydrogen radicals play an important role in e.g. the cleaning of EUV reflective mirrors. Therefore there is the need to quantify the surface radical flux in the various (plasma) setups where these effects are studied. In this paper a catalytic radical sensor is presented, based on the measurement of the recombination heat of radicals on a surface, using dual probe thermopile Heat Flux Sensors (HFS). The first HFS1 has a high recombination (probability) coefficient coating, e.g. Pt. The second HFS2 has a low recombination coefficient coating, e.g. Al2O3. Signal subtraction largely eliminates common mode heat losses/gains such as conduction/convection and IR-radiation, the net result representing the radical recombination heat. The signal can be improved by switching the radical source on/off at regular intervals. Radical recombination rates where measured in a remote microwave (MW) plasma chamber (38 Pa H2) over the range 1E18−1E21 atH/(m2s), with nearly linear response as function of plasma power setting. The sensor full scale limit is ~1E23 atH/(m2s) and is dictated by the maximum allowable sensor surface temperature (<250oC).

10:00am **PS2+SE-FrM-6 Dielectric Toroidal Plasma Sources for Improved Plasma Resistance***, **Ilya Pokidov,*** MKS Instruments

A new sintered alumina toroidal plasma source has been developed that overcomes the limitations that a quartz or hard anodized coated aluminum alloy applicator have. This alumina ceramic applicator is implemented in R*evolution® toroidal remote plasma source (RPS) chassis replacing the quartz, which predominantly is used in photoresist strip by oxygen plasma. The toroidal body is made of 99.5% pure alumina, more resistant than quartz to harsh plasma chemistries, such as H, F and Cl. It can withstand higher ignition and operating voltages, allowing to ignite plasma directly in process gas. Ceramic alumina is a very pure material. Impurities are below 0.5% versus the hard anodized coating typically grown from the base 6061 alloy with impurity content of up to 4.2%. The ceramic extends the principal limitation of quartz in handling halogen and hydrogen plasmas.

The torus is fabricated by first machining two identical halves in green state and then co-firing them together to form a high strength hermetic bond. Afterwards, the alumina torus' exterior surface is surrounded by a potting compound with high thermal conductivity and low elastic modulus and encapsulated inside a copper cooling jacket to minimize thermo-mechanical stress on the ceramic.

Tests of the alumina ceramic applicator indicate that it can safely operate up to 6kW, full range of R*evolution RPS power without fracturing. Plasma successfully ignited in process gases such as O_2/N_2, H_2, and N_2/H_2 with healthy operating windows. The alumina applicator underwent a 1000-hour life test in forming gas plasma without significant signs of surface erosion. Similar construction methodology is applicable to sapphire. However, a prototype sapphire torus has shown a lower operating power range than the alumina torus.

The paper will present the design methodology to address key technical challenges in the development of a dielectric toroidal applicator for a transformer coupled remote plasma source. Test data will also be presented to demonstrate operating windows and radical output capabilities of the ceramic toroidal remote plasma source in different gas chemistries.

10:20am **PS2+SE-FrM-7 What We Still Won't Know About Plasmas in Simple Diatomic Gases- or Using a DC Glow Discharge in Pure O_2 as an Ideal Test-Bed for Experimental Validation of Models*, Jean-Paul Booth*[1]*,*** LPP-CNRS, France **INVITED**

Despite many decades of study, models of discharges in molecular gases still lack accurate data on many key collisional processes, even for such "simple" and ubiquitous gases as O_2. Good data is lacking for near-threshold electron-impact dissociation with neutral products, the role of metastables; of gas heating, vibrational excitation and energy transfer processes; as well as surface recombination and thermal accommodation. Direct measurement of the rate constants of individual processes is a fastidious process, where it is even possible. As an alternative approach, we compare comprehensive measurements of internal plasma parameters to simulations for a plasma with relatively simple chemistry, namely a DC positive column discharge in pure O_2. This well-characterized, stable and uniform discharge is optimal for experiment-model comparison. Although this system has been studied for a many decades, new experimental methods, including synchrotron Vacuum ultraviolet absorption spectroscopy and laser cavity ringdown absorption spectroscopy (CRDS), allow the densities of all the major species (atomic, molecular, in ground and excited states) to be measured, with much-improved absolute accuracy, and with time resolution. The gas translational temperature, and vibrational energy distribution, were also probed. Applied to (partially- and fully-) modulated discharges, these measurements provide unprecedented insight into the kinetic processes occurring, and a profound test of the models. Whereas models can be quite easily adjusted to fit steady state measurements at one given set of operating conditions, trends with pressure and discharge current, and especially the temporal response to current modulation, are much harder to reconcile. In practice, model failures can often be attributed to simple omission of key processes, or to the neglect of their temperature-dependence. If the chemistry studied is simple enough, and the measurements cover all of the principal species (stable molecules in their ground and metastable states, atoms and negative ions) as well as the gas temperature, it becomes possible to identify the missing reactions, and even estimate their rates and activation energies, by adjusting their values in the model to fit the observations. As examples, we have demonstrated that the kinetics of metastable O_2 b molecules cannot be modelled without the inclusion of quenching by oxygen atoms with a significant activation energy. We have also demonstrated the production of ozone by the reaction of O_2 molecules with oxygen atoms chemisorbed on the glass discharge tube walls.

11:00am **PS2+SE-FrM-9 Voltage and Sheath Dynamics in Electropositive Capacitively Coupled Plasmas with Focus Ring and External Circuit*, Yuhua Xiao,*** *J. Brandon, J. Morsell,* NCSU*; S. Nam, J. Lee,* Samsung Electronics Co., Inc., Republic of Korea*; S. Shannon,* NCSU

Capacitively coupled plasmas (CCPs) are widely used in semiconductor processes. The control of plasma to obtain uniform deposition and etching over a large process space is still an open problem, particularly within a few millimeters of the substrate edge. Complex material stacks commonly referred to as focus rings (FR) or process kits are placed at the wafer edge to balance process non-uniformities and provide uniform process to the edge of the substrate. This solution has limitations with regard to process window and eventual material erosion.One promising approach is to combine a focus ring assembly with a tunable external circuit (EC) ground path termination to extend the plasma uniformity to the wafer edge over a wider process space. The effect of FR combined with EC for fine adjustment and minimization of edge process area are presented here. In this work, a simplified FR with EC structure consisting of a variable capacitor and an inductor is adopted to change the impedance between electrodes and the ground, and the sheath voltage distributions and width are modified. Experimental results are measured using hairpin probe, high-voltage RF and DC probes, in-line RF metrology at the powered electrode, and intensified CCD camera imaging of the electrode edge and FR region. The results are further compared to simulations, which use an equivalent circuit model to simulate the effect of this structure on sheath properties. Results show that the FR with EC structure can partially control the DC self-bias and distribute the voltage and the energy loss among different sheaths associated with different electrodes. The EC can affect the sheath dynamics and equipotential lines of the center and near the wafer edge prominently. These results point to possible source design based pathways for engineering the distribution of power dissipation across these sheaths in industrial plasma reactors to improve process performance at the electrode edge.

11:20am **PS2+SE-FrM-10 Time Resolved Diagnostics of a Silver HiPIMS Discharge*, Zachary Jeckell,*** *D. Barlaz, R. Ganesan, D. Kapelyan, K. Martin,* University of Illinois at Urbana Champaign*; W. Huber, B. Jurczyk,* Starfire Industries LLC*; D. Ruzic,* University of Illinois at Urbana Champaign

This work aims to investigate the temporal evolution of a high-power impulse magnetron sputtering (HiPIMS), with a positive cathode reversal, discharge by using the Hiden ANALYTICAL PSM probe, that can measure the ion energies as well as perform charge to mass (q/m) measurements. This allows for time resolved differentiation between the working gas and the sputtered material, which in this case is silver, and enables the quantification of the population of ions at higher charge states. Q/m differentiation allows for the construction of Ag^+/Ar^+, which when combined with previous IEDF measurements can help tailor future depositions to maximize the flux of silver ions. Our previous work studying the time evolution of the IEDF showed the peak energy of the distribution shifts to the set positive pulse voltage within 3 us regardless of conditions, and that there is a clear difference in the distribution during the first 20 us of the cathode reversal and the end of the cathode reversal, which we attributed to a higher presence of metal ions that are ionized in flight. This work would aim to verify this claim as well as quantify the population of silver in higher charge states. Investigating the population of Ag^{2+}, and other higher level charge states, is of interest because it is believed to lead to film damage for cases of large positive pulse biases, as the energy of the ions will likely be in the etching regime on the HiPIMS structural zone diagram. Multi-ionization results will be compared with fast camera measurements to see if the population of higher order charged states are correlated to the presence of hot spots. The fast camera measurements are taken using the PI-MAX 4 camera with a selected gate width of 100 ns. Additionally, the ionization fraction of silver can be found and the correlation between measured ionization fraction and the deposition rate measured with a quartz crystal microbalance (QCM) can help to determine the fraction of ions that return to the target and self-sputter as well as the fraction of ions that are transported to the substrate.

11:40am **PS2+SE-FrM-11 Title: Curling Probe Analysis for Practical Measurement of Electron Density*, Daisuke Ogawa,*** *K. Nakamura, H. Sugai,* Chubu University, Japan

Optical monitoring is a powerful diagnostic tool for plasma processing, but it should be reminded that optical emission from plasma is still secondary information.As learned from a plasma textbook, photon emission results from many electron relaxations of excited species.Behind the relaxation processes, electrons play a role in transferring their energy to create the excited species. The reaction rate of such reactive species strongly depends on electron density and temperature.Therefore, electron monitoring can be a powerful processing diagnostic even in a practical plasma because electron information can be utilized to know radiative and non-radiative species.Aiming for practical use of electron diagnostic, we have developed a curling probe, one of the diagnostics for finding electron density in plasma with a microwave-range electrical resonance.Plasma has a smaller dielectric constant than vacuum, making resonant frequency smaller. The degree of the frequency shift indicates electron density in plasma. The curling probe utilizes the measurement principle, and in particular, the probe utilizes a slot antenna to obtain the resonance.Due to the regulation of the probe space, the antenna is spiral-shaped and configured in a plane.So, the antenna configuration has some unique characteristics, which are not found in other microwave resonating probes, such as a hairpin probe. One of the unique characteristics of the probe is that the probe has a directionality of electron density measurement.We currently consider that the probe enables us to include the probe into an electrode.This

[1] **2019 PSTD Plasma Prize Winner**

configuration is possibly applied to a narrow-gaped capacitively coupled plasma. Our former work showed that the probe is getting ready for practical use because the probe operates under film depositing situations (Ogawa et al., PSST 30 (2021) 085009) with high pressure (<1000Pa). However, the probe still needs to be improved because we have noticed that the probe temperature affects the degree of the resonant frequency shift.We recently measured and analyzed the probe temperature and degree of resonant frequency shift, and found that the resonant frequency shift has a regularity in temperature. The regularity successfully enabled us to calibrate the probe measurement and showed that the probe is ready to utilize temperature-varying situations.This presentation will show our recent progress in electron density measurement with a curing probe under the temperature-varying situation.This presentation will provide an opportunity to discuss how to apply the probe to an industry reactor.

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