

# Tuesday Evening Poster Sessions, October 23, 2018

## Plasma Science and Technology Division Room Hall B - Session PS-TuP

### Plasma Science and Technology Division Poster Session

#### PS-TuP-1 Surface Modification for the Enhancement of the Patterning Margin by Using Plasma Treatment, *Wanjae Park, L Huli, S Chae, A Ko, P Biolsi*, TEL Technology Center, America, LLC

Extreme ultraviolet (EUV) lithography has been investigated to extend lithographic technology beyond its optical limits and replace current photolithography methods to pattern tiny critical dimension (CD) features. As the feature size is reduced, the adhesion between photo resist (PR) and its under layer such as silicon containing anti-reflective coating layer (Si-ARC) is getting worse. Recently, one of issues of EUV process is pattern collapse or flop-over phenomena that may ultimately render the substrate useless. This pattern collapse may be more observed, as the feature size is smaller due to smaller contact surface topographically. In this study, we carried out plasma treatments by using various gases on the under layer of PR which is Si-ARC, before PR coating. The CH<sub>4</sub> plasma treatment remarkably improves the pattern collapse phenomena. This surface modification effect as following as plasma chemistries was characterized by Fourier Transform Infrared Spectroscopy (FTIR), X-ray Photoelectron Spectroscopy (XPS) and Contact Angle measurement. From the FTIR analysis, we can detect additional Si-CH<sub>3</sub> peak (around 1261cm<sup>-1</sup>) after CH<sub>4</sub> plasma treatment on Si-ARC. The chemically bond Si-(CH<sub>3</sub>) groups might be thought as forming a hydrophobic surface while the surface oxidation was suppressed, which was proved by XPS results and Contact Angle results. Finally, the CH<sub>4</sub> plasma modifies hydrophilic property of the under layer of PR to hydrophobic surface thus enhancing the adhesion to PR. The benefit of increased adhesion results substantial improvements on production yield and enlarges the margin of Litho process window. This study will be helpful in enhancing the margin of EUV lithography process window and improvement on production yield for the manufacturing of Nano metric devices.

Keywords: Line Pattern Collapse, Surface Modification, Plasma Treatment, CH<sub>4</sub> Plasma, Contact Angle

#### PS-TuP-2 N<sub>2</sub>/H<sub>2</sub>, O<sub>2</sub> and NF<sub>3</sub> Dissociation Percentages in a Remote, Low Frequency, High Density Plasma Source, *Yingliang Zhou, H Li, V Donnelly*, University of Houston; *J Chiu, X Chen*, MKS Instruments, Inc., Pressure and Vacuum Measurement Group

Remote plasmas are drawing increasing attention for applications including chamber cleaning, chemical vapor deposition (CVD), surface modification and isotropic etching. The process is purely chemical in nature, with no surface damage from ion bombardment. The dissociation and recombination rates in the plasma source determine the reactive species fluxes delivered to the downstream chamber. The presentation will focus on measurements of percent dissociation of source gases commonly used in chamber cleaning and flowable CVD processes. Mixtures of N<sub>2</sub>/H<sub>2</sub>, O<sub>2</sub>, and NF<sub>3</sub> feed gases with Ar were delivered to the plasma at 400 sccm total flow rate and pressures of 0.4-4.0 Torr. The purely inductive, low frequency (400 kHz), toroidal plasma source (MKS Instruments) operates at a power density of 5 – 50 W/cm<sup>3</sup>. Radical densities and feed gas dissociation percentages in the plasma were measured by UV-visible optical emission spectroscopy (OES), combined with Ar actinometry. Effluents from the plasma source flowed into a downstream chamber that was equipped with a Deuterium lamp and a VUV spectrometer, for absorption spectroscopy measurements. The dissociation of O<sub>2</sub>, NF<sub>3</sub> and N<sub>2</sub>/H<sub>2</sub> gases in the plasma source will be compared to those measured downstream as a function of added Ar, total flow rate, discharge current, relative electron density and other plasma parameters.

#### PS-TuP-3 Thermal Atomic Layer Etching of Silicon and Silicon Nitride Using an Oxidation and "Conversion-Etch" Mechanism, *Aziz Abdulagatov, S George*, University of Colorado at Boulder

The thermal atomic layer etching (ALE) of silicon (Si) and silicon nitride (SiN) was performed using an oxidation and "conversion-etch" mechanism. In this process, the Si or SiN surface is oxidized to a silicon oxide layer using O<sub>2</sub> or ozone. The silicon oxide layer is converted to an Al<sub>2</sub>O<sub>3</sub> layer using trimethylaluminum (TMA). The Al<sub>2</sub>O<sub>3</sub> layer is fluorinated by HF to an AlF<sub>3</sub> layer prior to the removal of the AlF<sub>3</sub> layer by ligand-exchange using TMA. Si ALE was studied using silicon-on-insulator (SOI) wafers and SiN was examined using LPCVD SiN films. These investigations were performed in a warm wall reactor with a hot sample stage. *In situ* spectroscopic

ellipsometry was employed to monitor the thickness of both the Si or SiN film and the silicon oxide layer during ALE.

These studies observed that the Si and SiN film thickness decreased linearly with number of reaction cycles while the silicon oxide thickness remained constant. Using an O<sub>2</sub>-HF-TMA reaction sequence, the Si ALE etch rate was 0.4 Å/cycle respectively at 290°C. This etch rate was obtained using static reactant pressures of 250, 1.0 and 1.0 Torr, and exposure times of 10, 5 and 5 s, for O<sub>2</sub>, HF and TMA, respectively. The order of the reactant sequence affected the Si etch rate. Changing the reactant sequence from O<sub>2</sub>-HF-TMA to O<sub>2</sub>-TMA-HF reduced the etch rate from 0.4 to 0.2 Å/cycle at 290°C. Comparable etching rates were observed using ozone instead of O<sub>2</sub> as the oxidant. Comparable etching rates were observed for SiN ALE under similar reaction conditions. The Si and SiN ALE etch rates decreased with process temperature. An oxide thickness of ~10 Å remained after ALE at 290°C. However, this oxide thickness could be removed by sequential TMA and HF exposures without influencing the underlying silicon film.

These new thermal Si and SiN ALE processes are expected to yield isotropic etching. Thermal Si and SiN ALE should be useful in advanced semiconductor fabrication. Thermal Si ALE could also be utilized for atomic-scale polishing and cleaning of silicon surfaces. In addition, there may be applications in other areas such as silicon-based optoelectronics, photonics and MEMS fabrication. Thermal SiN ALE could be utilized in a broad spectrum of IC applications where SiN commonly used as an etch stop and diffusion barrier.

#### PS-TuP-4 Annihilation Kinetics of Plasma-induced Electronic Defects in Semiconductor Materials, *S Nunomura, Isao Sakata, K Matsubara*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

In semiconductor devices such as transistors, memory, solar cells, and light emitting devices, the electronic defects strongly impact on the device performance and reliability. These defects are often generated during the device fabrication, in which plasma processing technology is widely used for deposition, etching and implantation. To remove the defects in the devices, an annealing treatment is usually performed. However, some defects remain in the devices, and they deteriorate the device performance. The reduction of these residual defects is required, and thus it is important to understand the annihilation kinetics during the annealing period.

We studied the annihilation kinetics of electronic defects in hydrogenated amorphous silicon (a-Si:H). The electronic defects were generated by photon irradiation and plasma treatment. The annihilation of defects during the annealing is observed by in-situ photocurrent measurement [1-2]. An increase in the photocurrent reflects the annihilation of the defects. From the time evolution of the increasing photocurrent, we obtained the characteristic time,  $\tau$ , and an Arrhenius plot is prepared to determine the activation energy.

From the experiments, we find the following [3]. (i) The time evolution of the photocurrent exhibits the stretched exponential behavior, indicating the dispersive nature of a-Si:H. (ii) An Arrhenius plot shows an exponential decay of  $1/\tau$  vs  $1/T$ , verifying defect annihilation due to the thermal activation. Here,  $T$  is the annealing temperature. (iii) The activation energy is different, depending on the origin of defect generation. It is smaller for the defects generated by plasma treatments, compared with that of the defects induced by the photon irradiation. (iv) The exponential prefactor is different between the UV and VUV photon-induced defects. The details of the experimental setup, results and discussion will be given in the presentation.

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[1] S. Nunomura, I. Sakata, and M. Kondo, *Appl. Phys. Express* **6**, 126201 (2013). [2] S. Nunomura and I. Sakata, *AIP Advances* **4**, 097110 (2014). [3] S. Nunomura et al., submitted.

#### PS-TuP-5 High efficiency Magnetic Induction Plasma Source for Remote Plasma Removal Process, *TaeSeung Cho, S Park, D Lubomirsky*, Applied Materials

Selective material removal by using remote plasma becomes an indispensable process for 3D structures of semiconductor. In selective material removal process by remote plasma, the wafer process regime is completely isolated from the plasma source by perforated metal plates such as showhead. The radicals generated by electrical discharge pass through the perforated metal plate, while the charged particles cannot pass through. Thus, in the wafer process regime, the specific radicals from

# Tuesday Evening Poster Sessions, October 23, 2018

the remote plasma react with the target material to be removed from the wafer. Since the charged particles are screened by the plate, the damages by energetic charged particles can be drastically reduced. Therefore, the plasma source for remote plasma removal process should have features of (1) efficient radical generation with higher dissociation rate and (2) less charged particle leakage to wafer process regime.

Magnetic induction plasma concept is being used for lighting bulbs as well as Tokamak fusion reactor for several decades. Especially, the magnetic induction lighting and its driving electronics is being optimized for many years. Since the magnetic induction lighting doesn't have any electrode inside the bulb there's no particles from the electrode sputtered by energetic ions. In addition, magnetic induction plasma source as an inductively coupled plasma has higher dissociation rate compared to typical capacitively coupled plasma. Thus, introducing the magnetic induction lighting and its driving technologies to remote plasma removal process would make removal process more efficient and reliable with reduced cost of ownership.

Prototype chamber for magnetic induction plasma source for remote plasma removal process was assembled with standard KF flanges that could be brought off the shelf. To generate stable plasma, we modified the commercial electronic ballast. We introduced initial plasma generation concept to avoid the ignition failure which was one of the most common issue of magnetic induction plasma source. For preliminary study with the electrical and optical diagnostics, Ar+N<sub>2</sub> plasma was successfully generated/modulated in the chamber by using the ballast with wide operating pressures from 50mTorr to 200Torr.

**PS-TuP-6 Aspect-ratio and Line-edge Fluctuation Controlled Nanolithography using Poly(styrene-*b*-Dimethylsiloxane) and Amorphous Carbon Layer, JiSoo Oh, G Yeom, Sungkyunkwan University, Republic of Korea**

Of the various alternative lithography technologies, direct self-assembly (DSA) patterning technology using block copolymer (BCP) has received great attention due to excellent pattern resolution, process simplicity, low cost, and long-range ordering (good scalability).

Polystyrene-block-polydimethylsiloxane (PS-*b*-PDMS) with high Flory-Huggins interaction parameter ( $\chi$ ) have been extensively studied because they provide ultra-fine patterning and improved pattern quality. However, due to the preferential segregating property of PDMS in air and PS interface, it is disadvantageous to vertical orientation and it is difficult to fabricate BCP patterns with high aspect ratio (HAR)

Here, we will introduce the process of effectively pattern transfer by inserting an amorphous carbon layer (ACL) between the PS-*b*-PDMS BCP patterns and the underlying silicon substrate. In this study, we have overcome limitations of PS-*b*-PDMS BCP patterns with low aspect ratios by developing an etch selectivity close to infinity using plasma etch process. The PDMS patterns of various shapes could be fabricated into lamellar, rod, hole pattern with HAR by pattern transfer to ACL due to high etch selectivity plasma process. Also, line edge roughness (LER) and line width roughness (LWR) was improved due to the plasma trimming effect.

**PS-TuP-7 Development of A Low-Cost ZnO Nanorods-Based Gas Sensor with an Integrated Microplasma Generation Unit for Ethanol Sensing, Sz-Yun Lin, F Huang, C Hsu, National Taiwan University, Taiwan, Republic of China**

ZnO-based materials have been widely used as the gas sensing elements. The major limitations for this type of materials are the need to operate in high temperature or the requirement of the annealing step for fabrication or re-condition.

In this work, we developed a ZnO nanorods-based gas sensor integrated with a microplasma generation unit (MGU) that allows for detection of ethanol vapors at room temperature. This device consists of a specially-designed electrode set was fabricated using toner transfer method. This allows for the operation of microplasma generation mode(MGM) and gas sensing mode(GSM). After the fabrication of the 3-electrode set, ZnO nanorods was grown by hydrothermal method for 24 hours between two electrodes. ZnO-nanorods was first treated using the plasma for 10 minutes by sensing test. By proper connection of the electrodes, the device can be operated in GSM, which allows for ethanol vapor sensing test by measuring the resistance across the ZnO nanorods. The sensor is capable to detect a wide range of ethanol vapor, from 25 to 20000 ppm. In addition, the sensor shows excellent recyclability after repetitively testing for over 30 cycles. We will also show that the plasma treatment of the ZnO nanorods serves as

the regeneration of the sensing materials after the nanorods expose to humid air and loses their functionality for ethanol sensing.

This newly-developed integrated device offers a novel route for the development of sensing devices that allows for plasma treatment of sensing materials in-situ and on-site.

**PS-TuP-8 Development of a Plasma Generation Device Integrated with a Piezoelectric Spray to Detect Metal Ions in Solution, Ting-Ting Pan, S Lin, C Hsu, National Taiwan University, Taiwan, Republic of China**

In this work, we develop a system that contains a plasma generation device, a piezoelectric spray, and a spectrometer to detect metallic ions in solution. The plasma consists of a needle and a copper sheet as the anode and the cathode respectively. This plasma is driven by a homemade high voltage module that delivers 3 kV DC and is powered by a 5 V commercial portable power bank. The plasma is ignited in ambient air without the need of any purging gases. The mist of metal-ion-containing solution is sprayed to the plasma. The optical emission of the plasma is analyzed using a spectrometer for metallic element analysis. Such an arrangement allows for analysis of solutions with a wide range of electrical conductivities.

It is shown that the addition of a ballast resistor in series of the high voltage module effectively limits the current and plays an important role for metal detection. Without the ballast resistor, no metallic emission line is observed, despite of the fact that the plasma shows very bright emission. With the use of a ballast resistor of proper resistance, plasma appears to be more stable and clear Na and Pb emission lines are observed when a solution containing 1000 and 10000 ppm of Na and Pb, respectively, is spray to the plasma. We also observe that the gap between the electrodes is very critical for plasma characteristics. With a gap smaller than 0.5 mm, the plasma exhibits stable (DC) IV waveforms, while it shows self-pulsing characteristics with a gap greater than 0.5 mm.

We will show the progress toward the ultimate goal of this work: development of a system to detect metal ions in solution by integrating the plasma and spray devices with a home-made low cost spectrometer, and control the system using a Raspberry pi, a portable computer. Such an integrated system is fully functionalized and standalone and allows for simultaneous detection of multiple metal ions using plasma spectroscopy.

**PS-TuP-9 Development of a Light-weight System for Detection of Metal Ions in Solutions Using Plasma Spectroscopy, Ching-Yu Su, S Lin, C Hsu, National Taiwan University, Taiwan, Republic of China**

This work presents the development of a light-weight system that allows for simultaneous detection of multiple metallic elements in solution using plasma spectroscopy. This system consists of a pin-to-surface-type plasma, driven by a home-made high voltage module, and an atomizer to spray test solution into plasma. The optical emission of the plasma is analyzed using a spectrometer. Such an arrangement allows for detection metallic elements in solution with wide range of electrical conductivity of the solution by analyzing the optical emission of the plasma. A stainless steel pin and a copper sheet serve as the anode and the cathode, respectively, of the plasma. This plasma operates under atmospheric pressure in ambient air. The high voltage module delivers 3 kV DC to ignite the plasma and is powered by a 5-V commercial portable power bank. The atomizer is a piezoelectric spray. The power source of this spray is connected in series with a bipolar junction transistor (BJT), which is driven by a function generator to modulate the on and off of the spray. When the metallic element-containing solution is sprayed to the plasma, metallic emission can therefore be acquired.

We have observed that the spray frequency and duty greatly influence the plasma behavior and therefore its optical emission. Proper modulation of the spray is the key to generate stable plasmas with clear metallic emission. When the spray is set at 1 Hz with 50% duty using solution with 1000 and 10000 ppm of Na and Pb, respectively, clear metallic Na and Pb emissions are observed. We will further analyze the temporal-resolved optical emission to better understand the interaction between the mist and the plasma.

Finally, we will also demonstrate the use of a Raspberry Pi, a low-cost and credit-card-sized computer, to synchronize the spray and the plasma, and its integration with a homemade low cost spectrometer to develop a standalone and fully-functional device for detection of metallic elements in solution.

# Tuesday Evening Poster Sessions, October 23, 2018

## **PS-TuP-10 Inductively Coupled Plasma Reactive Ion Etching of Nanometer-scale Patterned Copper Thin Films using Alcohol-based Gases, Jinsu Ryu, E Lim, D Park, C Chung, INHA University, Republic of Korea**

Copper has been known as the next-generation interconnect materials in the metallization layer beyond the ultra large scale integration. Recently, the conventional aluminum interconnect materials needs to be replaced by copper which has many advantages compared to aluminum: high conductivity, less susceptible to electromigration, and lack of hillocks formations.

Copper thin films could not be patterned by the previous patterning techniques of photoresist masking and plasma etching that had been used with great success with aluminum. The inability to plasma etch the copper films called for the development on new etching technique. At last, it lead to a unique patterning process referred to as an additive patterning, also known as a 'Damascene' or 'dual-Damascene' process by analogy to a traditional technique of metal inlaying. However, as the critical device dimensions keep shrinking, the thickness of copper interconnect also should be decreased. This shrinkage in the copper thickness cause several issues in the copper patterning, which contain the increase in the resistivity of copper interconnect due to the increase in the resistivity of barrier layer and the change in grain size. There were many etching studies on the copper thin films using halogen-containing gases ( $\text{Cl}_2$ ,  $\text{HBr}$ ), hydrogen, and some organic materials, and all of their results were not satisfactory to apply to the copper patterning.

In this study, we will introduce an etching process of copper thin films using high density plasma etching in alcohol-based gases. The etch characteristics such as etch rate and etch profile will be presented as a function of gas concentration. Then the systematic parameter variation will be performed to improve the etch profiles. Finally, the etch mechanism will be investigated using X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDS). In addition, the plasmas properties will be analyzed using optical emission spectroscopy (OES) and Langmuir probe.

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## **PS-TuP-11 Etch Characteristics of Nanometer-scale Patterned Cu Thin Film Using Pulse-modulated RF Source Plasma, Euntaek Lim, J Ryu, C Chung, INHA University, Republic of Korea**

The critical dimensions of the semiconductor devices have been shrunk for better performance and functionality. As the minimum feature length keeps decreasing, the aluminum metal electrodes and wiring can not be used anymore and the need to use copper wiring instead of aluminum is increasing. Copper has very low resistance and high electromigration resistance, so the copper thin films is known as an excellent interconnect material compared to aluminum although the copper is more expensive than aluminum. In order to apply copper films into the interconnect, the patterning and etching process of copper films should be developed. Up to date, the studies on etch characteristics of copper thin films were performed using  $\text{Cl}_2$ ,  $\text{HBr}$ , and  $\text{H}_2$  gases but the satisfactory results were not obtained.

In this study, the pulse-modulated RF plasma etching of copper thin films has been introduced to achieve good etch results such as proper etch rate and good etch profile compared to those by the conventional continuous wave (CW) plasma etching which can produce low etch selectivity, etch residues, and poor etch profiles. This modulated plasma can provide the specific plasma conditions modified by special matching system that can change on-off duty ratio of 13.56 MHz RF power and frequency on the specific duty ratio. Currently, no good etch gases have been known to etch copper thin films. In this research, etching characteristics of copper thin film masked with nanometer-scale patterns was investigated in carboxylic acid using pulse-modulated inductively coupled plasma reactive ion etching (ICP RIE). The effects of on-off duty ratio and frequency of pulsed plasma on the etch characteristics of copper were examined.

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## **PS-TuP-12 Etch Characteristics of Magnetic Tunneling Junction Materials by Using Noble Gas and Hydrogen, SooGang Kim, K Yang, Y Shin, D Sung, G Yeom, Sungkyunkwan University, Republic of Korea**

As next generation non-volatile memory device, spin transfer torque magnetic random access memory (STT-MRAM) is one of the prospective

memory devices. But anisotropic etching of magnetic tunneling junction material (MTJ) is very difficult especially in nano-scale. Ar ion beam etch (IBE) not only has low etch selectivity but also induces sidewall re-deposition. Even though tilted ion beam can remove deposited materials at sidewall, a shadow effect restricts the effective removal of deposited materials in nano-scale pitch size. Some chemical reactive ion etching (RIE) can improve problems of Ar IBE, but they show other problem such as low selectivity, corrosion and chemical damage to magnetic materials.

In this study, MTJ materials were etched by using  $\text{H}_2$ , Ne, Ar and Xe inductively coupled plasma (ICP) and observed their etch characteristics. The nano-scale patterned MTJ material sample which is composed of  $\text{CoPt}(10\text{nm})$ ,  $\text{MgO}(1\text{nm})$ ,  $\text{CoFeB}(10\text{nm})$  with W hardmask was used for comparing etch profiles with re-deposition. The results show that  $\text{H}_2$  and Ne etch showed better etch profile and higher etch selectivity of MTJ materials over W than those with Ar. With Xe, etch selectivity was lower than the other gas, even though Xe showed an anisotropic profile. Also using the vibrating sample magnetometer (VSM), we compared saturated magnetic moments (Ms) to identify magnetic degradation. The patterned sample etched with Ne and Ar showed similar Ms, which means no significant magnetic degradation when using Ne.

## **PS-TuP-13 Particle Temperature Histories in a Tubular Low Temperature Plasma Reactor: Relevance to the Synthesis of Amorphous Metal Alloys, N Uner, Elijah Thimsen, Washington University in St. Louis**

The nonequilibrium environment of low temperature plasma (LTP) allows it to incorporate a significant amount of specific free energy to materials with which it is in contact. It has been shown recently that LTP is capable of synthesizing materials that are far away from equilibrium, as in the case of hyperdoped silicon nanocrystals [1]. Furthermore, LTP can also process pre-synthesized materials in such a way that the material is pushed far away from equilibrium, as demonstrated with in-flight size focusing of polydisperse aerosols [2]. However, examples on the transformation of materials with equilibrium atomic structure to materials with non-equilibrium structure are scarce. In this work, we propose that the distinct nanoparticle (NP) temperature histories in tubular LTP reactors can be utilized to transform crystalline metals into amorphous metals. Spatial characterization of an Ar plasma in a capacitively coupled tubular reactor revealed the existence of a zone with sharply elevated ion density and gas temperature in the vicinity of the powered electrode. Theory suggests that such an intense zone would heat NPs to temperatures above 1000 K, and rapid cooling would follow as NPs leave the zone. In the characterized reactor, an aerosol processing scenario was simulated, where pre-synthesized crystalline NPs were sent into the LTP. Copper-zirconium ( $\text{CuZr}$ ), which is a well-established glass former and is of interest for low temperature electro-catalysis applications, was taken to be the particle material. Calculations showed that the temperature history of a NP is strictly dependent on diameter, and on the intensity of the zone.  $\text{CuZr}$  melted in the intense zone, and subsequent cooling of the melt in the low intensity plasma downstream lead to quenching rates on the order of  $10^5$  K/s, all while particles maintaining a unipolar negative charge. Quenching rates of this magnitude are known to be sufficient to arrest an amorphous atomic structure [3].

[1] Zhou Shu *et al.*, "Boron- and Phosphorus-Hyperdoped Silicon Nanocrystals," *Part. Part. Syst. Charact.*, vol. 32, no. 2, pp. 213–221, Aug. 2014.

[2] N. B. Uner and E. Thimsen, "In-Flight Size Focusing of Aerosols by a Low Temperature Plasma," *J. Phys. Chem. C*, vol. 121, no. 23, pp. 12936–12944, Jun. 2017.

[3] F. Gillessen and D. M. Herlach, "Crystal nucleation and glass-forming ability of Cu-Zr in a containerless state," *Mater. Sci. Eng.*, vol. 97, pp. 147–151, Jan. 1988.

## **PS-TuP-14 Building Tailored Chemistry Sets for Plasma Modelling using a Statistical Approach Embedded in an Online Engine, Sebastian Mohr, G Evans, A Dzarasova, Quantemol Ltd., UK; M Virdee, University College London, UK**

The Quantemol Plasma Chemistry Generator has been developed within the PowerBase project to explore the vast number of potential chemical species and reactions present in a variety of plasma systems. Advances in computational and experimental plasma science as well as the increasing demand for precise and complex etching/deposition patterns have resulted in the use of increasingly complex plasmas for both research and industrial applications. Critical to the understanding and development of such methods in the semiconductor industry, is the identification of important chemical species and reactions present in the plasma, often a resource and

# Tuesday Evening Poster Sessions, October 23, 2018

time intensive endeavour. The Plasma Chemistry Generator tool suggests chemical species, important reactions and cross-section data for a given mixture of feed gases (e.g. SF<sub>6</sub>/CaF<sub>4</sub>), helping researchers to curate self-consistent sets of chemical reactions that are specific to the system of interest. Firstly, constituent plasma species are obtained from the Quantemol Database of Plasma Chemistries (QDB) [1] based on the chemical composition of the feed gases. Potential reactants and products for a hypothetical reaction are combined iteratively from these species, obeying mass and charge conservation rules, to form sets of allowed chemical reactions. Classification of these reactions into different process types, using models of reactions already available in QDB, facilitates the selection of important reactions based upon process parameters, such as the pressure of the plasma or the input power required for the users' application. In the final step, rate coefficients and/or cross sections are obtained from QDB where available. In case of unknown coefficients/cross sections, a suggestion by analogy to similar reactions will be made. By significantly reducing the time necessary to assemble a chemistry set, the Quantemol Plasma Chemistry Generator provides quick fundamental insights into plasma chemistries, accelerating the development and optimisation of new plasma systems and their applications. Examples of generated chemistry sets will be presented.

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1] J. Tennyson et al, QDB: a new database of plasma chemistries and reactions, *Plasma Sources Sci. Technol.* **26** (2017) 055014

**PS-TuP-15 Easy Synthesis of Hybrid Laterally or Vertically Patterned Hydrophobic/Hydrophilic Surfaces using a Dielectric Barrier Discharge, Annaëlle Demaude**, Université Libre de Bruxelles, Belgique; *M Gordon*, University of California at Santa Barbara; *F Reniers*, Université Libre de Bruxelles, Belgium

The quest for obtaining smart materials with combined surface properties is driven by their many potential applications. Whereas the surface science community can now easily synthesize (super)hydrophilic or (super)hydrophobic surfaces, there is nowadays a specific interest for having stable surfaces where some spots are hydrophobic and some are hydrophilic, leading for instance to controlled chemistry at the hydrophilic part, leaving the hydrophobic part unchanged (this is particularly useful for biomedical applications where controlled adsorption of biological molecules can be requested)<sup>1</sup>. Similarly, for antibiofouling applications in marine environment, having layers alternating in depth an hydrophilic/hydrophobic behavior may lead to lower shell adsorption<sup>2</sup>. This type of multilayers coating can also find applications in the manufacturing of water filtration membranes<sup>3</sup>.

In this research, we present a simple approach for synthesizing such patterns using a combination of two precursors, namely propargyl methacrylate (precursor for hydrophobicity) and acrylic acid (precursor for hydrophilicity) injected in a dielectric barrier discharge (DBD) operating at atmospheric pressure. A thin PVC mask is used for the surface patterning of the coating. Various amounts of the two precursors are injected in the DBD, which runs with argon as the main operating gas. These two precursors can indeed lead to coatings exhibiting contact angles varying from 140° to 15°<sup>4</sup>

The samples are characterized by secondary ion mass spectrometry (SIMS), both in static and dynamic mode, X-ray photoelectron spectroscopy and water contact angle. Despite the strong similarities between the two precursors, SIMS unambiguously show alternating in-depth composition of specific fragments. Similarly, water contact angle (with a reduced water drop size) shows that surface patterning is easily obtained by DBD, with contact angles of ~130° in hydrophobic areas and ~25° in hydrophilic areas. An alternate approach, consisting in exposing selected areas of the hydrophobic coating to an oxygen containing plasma, leads to angle of ~130° and ~17°, respectively. Such patterns are stable with time, opening the route for potential applications.

References:

- 1) Ueda, E.; Levkin, P. A. *Adv. Mater.* **2013**, *25* (9), 1234–1247.
- 2) Xu, G.; Liu, P.; Pranantyo, D.; Neoh, K.-G.; Kang, E.-T. *ACS Sustain. Chem. Eng.* **2018**.
- 3) Kong, Y.; Lin, X.; Wu, Y.; Chen, J.; Xu, J. *J. Appl. Polym. Sci.* **1992**, *46* (2), 191–199.
- 4) Nisol, B.; Ghesquière, J.; Reniers, F. *Plasma Chem. Plasma Process.* **2016**, *36* (5), 1239–1252.

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**PS-TuP-16 Plasma-based Approach to Driving an Amorphous-To-Crystalline Phase Change in MoS<sub>2</sub> Grown on Polymers, S Walton, D Boris**, U.S. Naval Research Laboratory; *A Kozen*, American Society for Engineering Education; *Gary Kushto*, U.S. Naval Research Laboratory; *M Johnson*, National Research Council; *R Rai*, University of Dayton; *N Glavin*, Air Force Research Laboratory; *C Muratore*, University of Dayton

The ability to grow high-quality, continuous 2D transition metal dichalcogenides (TMDs) on polymer substrates is a prerequisite for commercial flexible devices based on these materials. Molybdenum disulfide (MoS<sub>2</sub>) is a promising 2D semiconductor due to its relatively high charge mobility and a direct band gap of 1.8 eV coupled with optical transparency and high mechanical flexibility. Recently, magnetron sputtering from pure TMD targets, such as MoS<sub>2</sub> and WS<sub>2</sub>, was used for growth of amorphous precursor films at room temperature on polydimethylsiloxane substrates. *Ex situ* laser annealing after film growth was then used to drive an amorphous-to-crystalline phase change. While successful, the phase change was limited to the area defined by the beam diameter. Rapid, large scale, *in situ* methods would be an attractive alternative to meet the demands for commercial scale manufacturing.

In this work, we discuss the development of a plasma-based approach to driving the crystallization of few-layer, amorphous MoS<sub>2</sub> on polymers. The amorphous MoS<sub>2</sub> was deposited, via magnetron sputtering of MoS<sub>2</sub> targets, on polydimethyl siloxane (PDMS) substrates. The films were then exposed to electron beam generated plasmas produced in pure and dilute argon backgrounds to drive crystallization. The use of electron beam generated plasmas are attractive since they are both scalable to large areas and deliver a large ion fluence with kinetic energies as low as a few eV. The ion energies can be raised using DC or RF biasing, allowing the system to be tuned to deliver the energy required to drive the phase transition but limit etching and damage to monolayer films. The treated films are characterized using Raman, XPS, and Kelvin probes and those results will be discussed in terms of operating conditions such as treatment times, operating gas mixture, and ion energy. This work was partially supported by the Naval Research Laboratory base program.

**PS-TuP-17 Atmospheric Plasma Deposition of Vanadium Oxide Thin Coatings on Cold and Heated Substrates, Antoine Remy**, Université Libre de Bruxelles, Belgique; *M Gordon*, University of California at Santa Barbara; *F Reniers*, Université Libre de Bruxelles, Belgium

Atmospheric plasma deposition of vanadium oxide thin coatings on cold and heated substrates

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Vanadium oxides present interesting applications in thermochromic devices, electronic components, optoelectronics sensors, battery electrodes and catalysis. They can be synthesized by chemical vapor deposition (CVD) [1], or by magnetron sputtering [2]. In this research, we report, to the best of our knowledge, the first synthesis of vanadium oxide with a reactive atmospheric dielectric barrier discharge. This approach allows the direct synthesis of oxide layers on a wide variety of substrates, starting from an organometallic precursor in the vapor phase. Vanadium(V) oxytriisopropoxide vapours were injected in a DBD operating with argon as the main plasma gas. Variable quantities of the precursor and of oxygen (from 50 mL/min to 100 mL/min), operating as secondary reactive gas, were introduced in the discharge, and the plasma power was varied from 40 W to 60 W.

The coatings were deposited at room temperature, or, thanks to a new home made internal heating device, at higher substrate temperatures (ranging from 373 K to 573 K). Some coatings were post-annealed in air at 573 K.

The samples were characterized by X-ray diffraction, X-ray photoelectron spectroscopy and Infrared Spectrometry, in the IRRAS mode, and the electrical characteristics of the plasmas were studied by a high voltage probe. It is shown that the plasma power decreases with the introduction of oxygen, but remains virtually unchanged when the precursor is injected. Although, according to XPS, a significant amount of carbon still remains

# Tuesday Evening Poster Sessions, October 23, 2018

embedded in the final coating in the normal conditions of operation, typical IR bands for  $V_2O_5$  at  $1020\text{ cm}^{-1}$  and  $850\text{ cm}^{-1}$  were observed for samples prepared with  $50\text{ mL/min}$  of oxygen flow and at  $300^\circ\text{C}$  of sample temperature. This is confirmed by the oxidation state of vanadium ( $V^{5+}$ ), as observed by the XPS peak at  $517.2\text{ eV}$ . The oxidation state seems to change with the conditions of the synthesis, starting from  $+5$  for the original precursor, going down to  $+4$ , and then reaching  $+5$  again for  $V_2O_5$ .

## References

- S. Wanga, K.A. Owusu, L. Mai, *Applied Energy* 211, p. 200–217, 2018.  
 [1] M. S.B. de Castro, C.L. Ferreira, R.R. de Avillez, *Infrared Physics & Technology* 60, pp. 103-107, 2013.

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**PS-TuP-18 The Increased Efficiency Of The Amorphous/Silicon Heterojunction Solar Cells With Silicon Micro-Channels In Back Side Substrate, Hugo Alvarez, G Bertão, A Silva, F Ciodin, J Diniz,** University of Campinas, Brazil

In this work, silicon based heterojunction (SHJ) solar cells were fabricated without a intrinsic layer using a  $200\text{ nm}$  a-Si:H  $p^+$  layer deposited by Electron Cyclotron Resonance-Chemical Vapor Deposition (ECR-CVD) system on to  $p^+$ -c-Si substrate. The electrical parameters of the obtained solar cells, such as efficiency, are related to the effects of: i) radio-frequency (RF) chuck power, used during the deposition of amorphous silicon (a-Si:H) Electron Cyclotron ECR-CVD, in the incorporation of H into the a-Si:H films for different RF powers; ii) Silicon micro-channels, which were fabricated in the back-side substrate with the solar cells.

The films were deposited using a ECR power of  $500\text{ W}$ , pressure of  $4\text{ mTorr}$ , substrate temperature of  $20^\circ\text{C}$ , gas flows of  $\text{SiH}_4$  and Ar,  $200$  and  $20\text{ sccm}$  and  $20$  minutes and RF power of  $1$ ,  $3$  and  $5\text{ W}$ . To create the  $p^+$  layer, the samples were boron implanted and annealed in a RTA process. Back and front aluminum contacts of  $500\text{ nm}$  were deposited by sputtering and a thin layer of silicon oxide for passivation and an antireflective coating of silicon nitrite was deposited in the ECR for PV Cells efficiency measurements. The back-side contacts were corroded in circular dots ( $200\text{ }\mu\text{m}$  of diameter) and used as mask to define the silicon micro-channels using ICP (Inductively Coupled Plasma) plasma etching based on  $\text{SF}_6/\text{Ar}$  gas mixture. This SHJ solar cells were fabricated and the current density versus voltage curves in illuminated (AM 1.5) condition were measured. Before the microchannel etching, all solar cells, presented lowest efficiencies of about  $0.001\%$ . After the formation of the Micro-Channels (depths of about  $7.5\text{ }\mu\text{m}$  and  $8.2\text{ }\mu\text{m}$ , for  $10$  and  $40$  minutes, respectively) using ICP plasma etching increased these values at least one order of magnitude. The maximum of  $0.4\%$  of efficiency was obtained for the SHJ cell, which was fabricated with the a-Si:H film of  $3\text{ W}$  RF power and with micro-channel in back-side, using  $10$  minutes of ICP etching. In the future, we intend to fabricate a microfluidic system to introduce the fluid into the Micro-Channels to cool and to increase the efficiency values of solar cells.

**PS-TuP-19 Effect of RF Plasma on H Radical Generation on DCMS Produced a-Si:H, Jan Uhlig, E Barlaz, D Ruzic,** University of Illinois at Urbana-Champaign

We report on the correlation between hydrogen radical concentrations and the densities of amorphous silicon produced by DCMS in Ar. Previously, the addition of molecular hydrogen during growth at pressures sufficient to produce viable inclusion rates frequently led to blister formation and potential delamination in the final film. An alternative approach demonstrated here is to improve the concentration of hydrogen radicals relative to molecular hydrogen through the use of a secondary plasma from an RF coil in the deposition chamber. At  $300\text{ W}$  RF power and  $1\text{ mTorr}$  of Ar, the addition of a fraction of a mTorr of hydrogen gas leads to a  $20\%$  reduction on film density. The relationship between hydrogen radical concentration production and secondary plasma power will be characterized by radical probe measurements.

**PS-TuP-20 Hardmasks of TiN and Al for Silicon Micro-Channel Definition via ICP Plasma Etching Process, Camila Ruiz,** Plasma Nanotechnology Research Center, UNICAMP, Brazil; J Diniz, A Rosa, Plasma Nanotechnology Research Center, University of Campinas, Brazil

TiN and Al films were used as hard mask (HM) materials in Si etching using a high-density inductively coupled plasma (ICP) reactor for silicon micro-channel (SiMC) (with depth  $> 1\text{ }\mu\text{m}$ ) fabrication. The main proposal on this research is define a best hard mask (HM) for silicon micro-channel (SiMC)

fabrication using ICP (Inductively Coupled Plasma) etching process. In addition, there are some important properties for hard mask should achieve, such as high mechanical performance and etch resistance to support the high process conditions. The TiN and Al films were deposited on silicon substrate by sputtering. Table 1 presents the obtained samples, with the thickness values and whether the annealing was performed or not.

**Table 1.** The obtained samples and the Hard Mask (HM) conditions  
**Table 2** The used ICP parameters (fixed conditions:  $P=30\text{ mTorr}$ ,  $450\text{ WICP}$ ,  $100\text{ WRIE}$ ) ICP Parameters (sccm)

Samples	HM	Thickness	Annealing	Process		Time(min)
				#	ICP Parameters (sccm)	
A	TiN	100nm	YES	#1	48SF6+87Ar	10
				#2	48SF6+87Ar	20
				#3	48SF6+87Ar	30
B	TiN	100nm	NO	#4	48SF6+87N2	10
				#5	48SF6+87N2	20
C	Al	100nm	YES	#6	48SF6+87N2	30
D	Al	100nm	NO	#7	First sequence:20seconds, 48SF6+87ArSecond	20
E	Al	500nm	YES	#8	sequence:20seconds,48C3F8+87Ar	20
F	Al	500nm	NO		First sequence:20seconds, 48SF6+87N2Second sequence:20seconds,48C3F8+87N2	

The ICP processes to fabricate the silicon micro-channels (SiMC) and to characterize the mask resistance under the plasma etching were carried out using these fixed parameters as table 2. Two different gas mixtures were used for etching steps without the environment changing:  $\text{SF}_6+\text{Ar}$ , and  $\text{SF}_6+\text{N}_2$  for  $10$ ,  $20$  and  $30$  minutes were employed. Two sequences of gas mixtures were used for etching steps in cycles with the gas environment changing: the first cycle was:  $20$  seconds  $\text{SF}_6+\text{Ar}$ , and in the sequence,  $20$  seconds, with  $\text{C}_3\text{F}_8+\text{Ar}$ ; the second cycle was:  $20$  seconds with  $\text{SF}_6+\text{N}_2$ , and in the sequence,  $20$  seconds, with  $48\text{ sccm}$  of  $\text{C}_3\text{F}_8+\text{N}_2$  for  $20$  minutes. The steps in cycles with different gas environments were based on Bosch process [1,2]. Usually, the Bosch process is performed using the cycles based on one sequence with  $\text{SF}_6/\text{Ar}$  gas mixture, with  $\text{C}_4\text{F}_8/\text{Ar}$ . In this work, we have used  $\text{C}_3\text{F}_8$  gas, instead of traditional  $\text{C}_4\text{F}_8$ . Table 2 shows the conditions of ICP etching processes. The TiN hard masks have presented high resistance to etching process. However, the  $100\text{ nm}$  Al films did not present high resistance, because the sputtering mechanism can occur. The  $500\text{ nm}$  thick layers (samples E and F, Table 1), have presented the high resistance to etching process.

**PS-TuP-21 Time- and space-resolved Diagnostics of a Self-Neutralized Ion Beam Extracted from a Pulsed Plasma, Ryan Sawadichai, Y Chen,** University of Houston; S Tian, Lam Research Corporation; V Donnelly, P Ruchhoeft, D Economou, University of Houston

Ion beams are extensively used in a variety of thin film deposition and etching technologies. To neutralize the space charge of a positive ion beam extracted from a plasma, hot filaments, emitting electrons thermionically, are strategically placed on the downstream side of the extraction grid. Charge neutralization prevents spreading of the ion beam by Coulomb collisions among the ions. This work reports our observation that a self-neutralized ion beam can be obtained when the beam is extracted in the afterglow of a pulsed plasma, in the absence of any hot filaments. Specifically, a nearly monoenergetic ion beam was realized by applying a synchronous DC bias on an electrode in contact with the plasma during a specified time window in the afterglow of a pulsed plasma. Interestingly, the ion beam flux in the pulsed plasma case was much higher than that in a continuous wave plasma, under comparable operating conditions. Time resolved measurements of the ion and electron energy distributions were performed along the beam axis to characterize the spatiotemporal evolution of the beam and arrive at a plausible explanation for self-neutralization. Near the grid, positive ions reach a peak current during the active glow, and again soon after the application of bias in the afterglow, while electron current peaks only at the beginning of the afterglow. At distances greater than  $10\text{ cm}$  away from the extraction grid, ions are only detected after the application of bias at a peak current with a delay corresponding to the flight time, while the electron peak did not shift. The time- and spaced-resolved measurements support a mechanism in which electrons from a low-density plasma near the ion extraction grid neutralize the space charge in the transiting beam.

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# Tuesday Evening Poster Sessions, October 23, 2018

**PS-TuP-22 Vacuum-ultraviolet-radiation Damage of Low-k Dielectrics, J. Leon Shohet, S Kim, H Nguyen, P Xue, J Blatz, H Cheng, University of Wisconsin-Madison; Y Lin, NSRRC, Taiwan; J de Marneffe, M Redzheb, S Armini, IMEC, Belgium; C Chen, NSRRC, Taiwan; Y Wu, University of Wisconsin-Madison**

VUV exposure of dielectrics during processing can cause damage and can also be beneficial. The goal of this work is to optimize the "beneficial" spectrum of photon radiation during plasma processing. To fully separate the effects of charged-particle bombardment a synchrotron can be used to provide a continuous spectrum of radiation over the range that most processing plasmas generate. In this work, four low-k samples were provided by IMEC. Their properties before exposure are as follows:

Precursor	Template	UV cure	k value at 100 kHz	
Sample 1	PMO	CTAC (C)	No	2.35
Sample 2	MSQ	BrijL4 (L4)	No	2.36
Sample 3	MSQ	BrijS10 (S10)	No	2.26
Sample 4	MSQ	BrijS10 (S10)	Yes	2.13

To determine the spectral effects of irradiation a five-step procedure was followed. The steps are (1) a rapid photon energy scan to measure the substrate current caused by photoemission as a function of photon energy. (2) Determine which photon energies generate the highest and lowest substrate currents. (3) Irradiate samples separately at the photon energy for the (a) the highest and (b) the lowest substrate current. (4) Measure the substrate current as a function of time for each of the monochromatic irradiations. (5) Following the monochromatic irradiation, a rapid photon energy scan was made again to determine whether changes could be observed in the dielectrics.

For each case, the substrate current begins at a high value and then decays as a function of time until it reaches a steady state. This is typically found after photoemission occurs because the dielectric acquires a net positive charge and thus photoemitted electrons tend to be attracted back to the dielectric. It should be emphasized that the substrate current does not decay to zero but reaches a constant value which is caused by photoinjection of electrons from the silicon substrate.

The damage effects were measured by examining the changes in dielectric constant, dielectric thickness, mechanical properties using nanoindentation, and chemical bond structures using FTIR. It was determined that VUV irradiation with photon energies  $> 7$  eV increased the concentration of silicon dangling bonds in low-k SiCOH. Photons of lower energy were not able to break the Si-O bonds that have a dissociation energy of 6.3 eV. TDDB degradation and negative mobile-charge generation were observed when the photon energy was greater than 9 eV. The k value increased when the dielectrics were exposed to photon energies  $> 8$  eV. VUV photon irradiation increased the film hardness at photon energies of 10.2 and 11.8 eV. The dielectric constant increased slightly after exposure for all samples.

**PS-TuP-23 Porous Alumina as a Vacuum Ultraviolet Transmission Window, Yuting Wu, H Cheng, University of Wisconsin-Madison; Y Lin, C Chen, H Fung, NSRRC, Taiwan; J Shohet, University of Wisconsin-Madison**

Porous alumina is examined as a coupling window between an electron-cyclotron-resonance plasma used as a vacuum ultraviolet vuv source and a separate processing chamber. The porous alumina sample coupon used in this work has the following properties. The sample is 2 x 2 cm. Its thickness is 38 microns. It is composed of pores that are 20 nm in diameter resulting in a porosity of 50%.

To eliminate the effects of particles, a synchrotron was utilized to obtain the transmission properties as a function of photon energy. The transmission of VUV through porous alumina was measured as a function of wavelength is measured and was found to be nearly 50%. A silicon wafer with a dielectric surface is then placed in the processing chamber and exposed to VUV, both with and without the porous alumina window. A Kelvin probe is used to measure the surface charge induced on the wafer by photoemission in both cases, which will determine whether porous alumina can efficiently couple the VUV irradiation to a sample in a processing plasma without significant modification to its spectrum and its resulting effects on the material. The advantage of porous alumina over a glass capillary-array window is that the hole diameters are in the nanometer range and this minimizes any particle flux compared with the glass capillary array.

**PS-TuP-24 Frequency Response of Microwave Excited Argon Microplasmas using Continuum Simulations, Ayyaswamy Venkatraman, A Verma, University of California Merced**

Scientific computing has emerged as an essential tool for the investigation and prediction of microwave sustained microplasmas for applications in metamaterials research. In this work, we intend to perform an in-depth numerical analysis of microwave microplasmas and present a broader scope of physical mechanism characteristics to microplasmas with an emphasis on frequency response of plasma dynamics. We will report two-dimensional fluid simulations of low-temperature microwave excited argon microplasmas in split ring resonators operating at or near atmospheric pressure. An in-house plasma solver is used to simulate these geometries in practical engineering conditions. Some salient features of these parallel simulations include the use of an unstructured mesh with both plasma and dielectric regions solved in a strongly-coupled manner. The simulations also utilized full-momentum equation for all species thereby doing away with possible approximations involved in the drift-diffusion approximation. We also present direct comparisons with experiments and drift-diffusion simulations performed by the Hopwood group in comparable geometries. The two-dimensional simulations will also be compared with previously published results using one-dimensional continuum and kinetic (particle-in-cell with Monte Carlo collision) simulations thereby quantifying the error associated with a one-dimensional approximation. Specifically, the frequency response predicted by one-dimensional simulations point to the existence of several interesting operating regimes depending on the excitation frequency in comparison to the collision frequency and the plasma frequency which will need to be compared with the predictions of the two-dimensional simulations (because of the ability of the plasma to expand). The feasibility of performing realistic two-dimensional/three-dimensional simulations of microwave microplasmas opens several possibilities in terms of optimizing the operating characteristics of these devices in various applications including plasma-based metamaterials.

**PS-TuP-25 Development of an In-situ Plasma Enhanced Atomic Layer Etching System for III-group Nitride Device Process, C.P. Lin, Y Lin, C Chen, M Wang, National Applied Research Laboratories, Taiwan, Republic of Korea; C Hsiao, National applied research Laboratories, Taiwan, Republic of Korea, Taiwan, Republic of Korea; F Chen, National Applied Research Laboratories, Taiwan, Republic of Korea**

An in-situ plasma enhanced atomic layer etching system has been design and fabricated. NO<sub>2</sub>, BCl<sub>3</sub> and Ar plasma were used as the precursor for AlGaN epitaxy layer at various temperature. The optical detector was used to in-situ monitor the plasma spectrum during the step by step etching process. It is found that the layer by layer etching feature shows the process is a controlled self-limited reaction. In addition, the saturation curve of etching rate and precursor pulsed time has been established. Furthermore, This system could be used for the III-group nitride semiconductor device process.

**PS-TuP-26 Advances in the Spectroscopic Characterization of Ceramic Films and Coatings, Fuhe Li, A Tavakoli, J Brim, Air Liquide Electronics - Balazs NanoAnalysis**

A variety of radio frequency (RF) plasma source atomic optical emission spectroscopy and atomic mass spectrometry have been developed and implemented in our laboratory to characterize various solid ceramic materials, thick coatings and metal-oxide thin films. The techniques that we have developed include but are not limited to glow discharge OES, ICP-OES, laser ablation ICP-MS. Utilizing advanced RF plasma or a high energy laser beam for material sputtering, excitation or ionization, many intrinsic limitations associated with Auger, EDS, GD-MS, RBS, and SIMS techniques such as surface charging are eliminated. The signal intensities produced by these advanced techniques all have a simple and well-defined mathematical (linear) relationship with elemental concentrations in the material. A wide linear dynamic range (over seven orders of magnitude) in these techniques coupled with traceable NIST material standards developed in our laboratory have made accurate surface, interfacial and bulk analyses possible. The advances have also led to a much higher sensitivity in impurity analysis and a much higher accuracy in compositional verification. In addition, deep depth profiling a  $> 50$   $\mu$ m hard and thick ceramic coating (e.g. Type III anodized coatings) throughout its entire thickness in a real-time fashion can now be accomplished.

# Tuesday Evening Poster Sessions, October 23, 2018

**PS-TuP-27 Effect of Plasma Configuration on Defect-free Functional Doping on Graphene Surface,** *Goo-Hwan Jeong, S Jo*, Kangwon National University, Republic of Korea

In this presentation, I will present the effect of plasma configuration on defect-free functional doping on graphene surface. The system is a vertical-type direct-current plasma with parallel electrodes. We change the electrode configuration and adjust the plasma input power and treatment time to utilize various ion-bombardment energies and plasma doses. The up-cathode system with a powered upper electrode and ground lower anode is more suitable than the traditional down-cathode system for efficient plasma doping. This configuration yields a low-energy ion process and thus suppresses high-energy ion-induced damages.

The graphene was prepared by mechanical exfoliation and the doping was performed using ammonia gas. The degree of a structural damage on graphene after the doping was mainly evaluated using Raman spectroscopy. Finally, the structural evolution of graphene and the doping components with respect to the plasma conditions are extensively characterized with Raman spectroscopy, atomic force microscopy, and X-ray photoelectron spectroscopy. In addition, we provide the results of *in-situ* OES analysis during plasma-doping process. The results provide an effective doping condition for doping nanomaterials without plasma-induced damage.

**PS-TuP-28 Fluid Model Numerical Simulation Analysis of Microwave Plasma Discharges,** *Wan-Ting Chiu*, National Tsing-Hua University, Taiwan, Taiwan, Republic of China; *I Yeh, K Leou*, National Tsing-Hua University, Taiwan, Republic of China

Microwave plasma discharges have been widely employed for diamond synthesis. In this work, fluid model numerical simulation analysis, using a commercial available code, COMSOL-Multi-physics, has been conducted for

microwave hydrogen plasma discharges operated at 2.45 GHz. The simulation model consists of all basic physical mechanisms, including electromagnetics, plasma discharge, gas flow and heat transfer, along with gas phase and surface reactions of gaseous species and charged particles.

For our first study, we investigated a plasma reactor based on the  $TM_{02}$  mode microwave applicator and a quartz dome. The simulation analysis was first employed to fine tune the structure dimension maximize the coupling of the 2.45 GHz microwave to the desired waveguide mode,  $TM_{02}$ , while minimizing its coupling to the major competing mode  $TM_{01}$ . The simulation analysis with plasma discharge shows that a plasma ball is formed above the substrate stage for certain operating conditions, while a separate plasma discharge appears if operated outside those operating "window", a common characteristics of microwave plasma discharge operated under microwave cavity resonator mode. Parametric analysis of plasma discharge characteristics for different gas pressure and microwave power have been carried out. Detailed simulation results will be presented.

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**PS-TuP-29 Evaluation of Simulation Tool for a Plasma Generation based on the Dual Property of Electrons,** *Shinichiro Kitamoto, P Abraha*, Meijo University, Japan

This research presents the development of a simulation tool that characterizes and optimizes the plasma characteristics of a new plasma device based on the dual property of electrons. The plasma device consists of three areas, namely the expansion area, the diffraction area, and the processing area. Successive electrodes generate, expand, and diffract the electrons that dissociate and ionize the nitrogen gas into a plasma. The device is specifically tailored to produce a uniform and large-volume plasma that can harden the surface of large mechanical parts or a large number of mechanical parts. Evaluation of the performance of the plasma device in attaining a uniform and large-volume treated materials requires extensive experimental work, modeling and numerical simulation in addition to plasma diagnostics. In this research, the principle of the plasma generation and the operating conditions of the plasma device are considered in constructing the simulation tool that illustrates the qualitative relations of the plasma parameters against the magnitude and uniformity of the plasma. Numerical simulation of three sequential regions namely particle, wave, and particle regions corresponding to the expansion, diffraction, and processing areas are modeled to give the total framework. The two particle regions, Particle-In-Cell and Monte-Carlo-Collision methods, are carried out to determine the particle energy and position within the plasma chamber. While in the wave region, the Fresnel theory is used to determine the diffracted electron intensity distribution. In

combining the results of the particle and wave regions, the plasma characteristics of the device are holistically determined. Comparison of the results of the simulation and experimental data obtained show good agreement, thus verifying the validity of the simulation tool.

**PS-TuP-30 Plasma Nitriding of Highly Polished Metallic Surfaces,** *Yoshiki Handa, P Abraha*, Meijo University, Japan

This research presents an appropriate plasma nitriding method for highly polished precision metallic components that need to maintain the as-finished surface conditions after the plasma treatment. Conventionally, a nitrided layer consists of a hard but brittle nitrogen compound layer and a layer made of diffused interstitial nitrogen atoms. The compound layers,  $Fe_{3-2}N$  (gamma-prime) and  $Fe_4N$  (epsilon) form when the phase field has a solubility range of about 6-8 percent weight nitrogen. A high concentration of the nitrogen atoms on the surface, or concentration gradient, drives the atoms along the grain boundaries of the sample to form the diffusion layer. In this research, the incidence of the electrically charged electrons and ions is controlled to suppress the formation of the gamma-prime and epsilon phase fields and maintain a steady flow of interstitial nitrogen atoms along the subsurface. In this configuration, the sample is set inside a shielding grid that is located in the electron beam excited plasma chamber. The shielding grid is a 40-mesh screen biased negatively, while the sample is biased positively. The negatively biased grid repels the electrons that cause overheating in addition to attracting the ions for possible charge exchange with the meshed wire, thus increasing the atom density. On the other hand, the sample is positively biased to avoid any incoming ions from approaching the sample. In this experiment, the driving parameters of the built-in bias configuration were optimized to guarantee a diffusion-based nitriding that suppresses the formation of the compound layer. A comparison is then made based on measurements of the plasma species that interact with the samples and the characteristics of the treated samples in using both the diffusion-based method, neutral nitriding, and the conventional ion nitriding method. The results show neutral nitriding is a successful nitriding method that can strengthen the surface while keeping the surface free of the compound layer.

## Author Index

### Bold page numbers indicate presenter

— A —

Abdulagatov, A: PS-TuP-3, **1**  
Abraha, P: PS-TuP-29, **7**; PS-TuP-30, **7**  
Alvarez, H: PS-TuP-18, **5**  
Armini, S: PS-TuP-22, **6**

— B —

Barlaz, E: PS-TuP-19, **5**  
Bertão, G: PS-TuP-18, **5**  
Biolsi, P: PS-TuP-1, **1**  
Blatz, J: PS-TuP-22, **6**  
Boris, D: PS-TuP-16, **4**  
Brim, J: PS-TuP-26, **6**

— C —

Chae, S: PS-TuP-1, **1**  
Chen, C: PS-TuP-22, **6**; PS-TuP-23, **6**; PS-TuP-25, **6**  
Chen, F: PS-TuP-25, **6**  
Chen, X: PS-TuP-2, **1**  
Chen, Y: PS-TuP-21, **5**  
Cheng, H: PS-TuP-22, **6**; PS-TuP-23, **6**  
Chiu, J: PS-TuP-2, **1**  
Chiu, W: PS-TuP-28, **7**  
Cho, T: PS-TuP-5, **1**  
Chung, C: PS-TuP-10, **3**; PS-TuP-11, **3**  
Ciodin, F: PS-TuP-18, **5**

— D —

de Marneffe, J: PS-TuP-22, **6**  
Demaude, A: PS-TuP-15, **4**  
Diniz, J: PS-TuP-18, **5**; PS-TuP-20, **5**  
Donnelly, V: PS-TuP-2, **1**; PS-TuP-21, **5**  
Dzarasova, A: PS-TuP-14, **3**

— E —

Economou, D: PS-TuP-21, **5**  
Evans, G: PS-TuP-14, **3**

— F —

Fung, H: PS-TuP-23, **6**

— G —

George, S: PS-TuP-3, **1**  
Glavin, N: PS-TuP-16, **4**  
Gordon, M: PS-TuP-15, **4**; PS-TuP-17, **4**

— H —

Handa, Y: PS-TuP-30, **7**  
Hsiao, C: PS-TuP-25, **6**  
Hsu, C: PS-TuP-7, **2**; PS-TuP-8, **2**; PS-TuP-9, **2**  
Huang, F: PS-TuP-7, **2**  
Huli, L: PS-TuP-1, **1**

— J —

Jeong, G: PS-TuP-27, **7**  
Jo, S: PS-TuP-27, **7**  
Johnson, M: PS-TuP-16, **4**

— K —

Kim, S: PS-TuP-12, **3**; PS-TuP-22, **6**  
Kitamoto, S: PS-TuP-29, **7**  
Ko, A: PS-TuP-1, **1**  
Kozen, A: PS-TuP-16, **4**  
Kushto, G: PS-TuP-16, **4**

— L —

Leou, K: PS-TuP-28, **7**  
Li, F: PS-TuP-26, **6**  
Li, H: PS-TuP-2, **1**  
Lim, E: PS-TuP-10, **3**; PS-TuP-11, **3**  
Lin, C: PS-TuP-25, **6**  
Lin, S: PS-TuP-7, **2**; PS-TuP-8, **2**; PS-TuP-9, **2**  
Lin, Y: PS-TuP-22, **6**; PS-TuP-23, **6**; PS-TuP-25, **6**

Lubomirsky, D: PS-TuP-5, **1**

— M —

Matsubara, K: PS-TuP-4, **1**  
Mohr, S: PS-TuP-14, **3**  
Muratore, C: PS-TuP-16, **4**

— N —

Nguyen, H: PS-TuP-22, **6**  
Nunomura, S: PS-TuP-4, **1**

— O —

Oh, J: PS-TuP-6, **2**

— P —

Pan, T: PS-TuP-8, **2**  
Park, D: PS-TuP-10, **3**  
Park, S: PS-TuP-5, **1**  
Park, W: PS-TuP-1, **1**

— R —

Rai, R: PS-TuP-16, **4**  
Redzheb, M: PS-TuP-22, **6**  
Remy, A: PS-TuP-17, **4**  
Reniers, F: PS-TuP-15, **4**; PS-TuP-17, **4**  
Rosa, A: PS-TuP-20, **5**  
Ruchhoeft, P: PS-TuP-21, **5**  
Ruiz, C: PS-TuP-20, **5**  
Ruzic, D: PS-TuP-19, **5**  
Ryu, J: PS-TuP-10, **3**; PS-TuP-11, **3**

— S —

Sakata, I: PS-TuP-4, **1**  
Sawadichai, R: PS-TuP-21, **5**  
Shin, Y: PS-TuP-12, **3**  
Shohet, J: PS-TuP-22, **6**; PS-TuP-23, **6**  
Silva, A: PS-TuP-18, **5**  
Su, C: PS-TuP-9, **2**  
Sung, D: PS-TuP-12, **3**

— T —

Tavakoli, A: PS-TuP-26, **6**  
Thimsen, E: PS-TuP-13, **3**  
Tian, S: PS-TuP-21, **5**

— U —

Uhlig, J: PS-TuP-19, **5**  
Uner, N: PS-TuP-13, **3**

— V —

Venkatraman, A: PS-TuP-24, **6**  
Verma, A: PS-TuP-24, **6**  
Virdee, M: PS-TuP-14, **3**

— W —

Walton, S: PS-TuP-16, **4**  
Wang, M: PS-TuP-25, **6**  
Wu, Y: PS-TuP-22, **6**; PS-TuP-23, **6**

— X —

Xue, P: PS-TuP-22, **6**

— Y —

Yang, K: PS-TuP-12, **3**  
Yeh, I: PS-TuP-28, **7**  
Yeom, G: PS-TuP-12, **3**; PS-TuP-6, **2**

— Z —

Zhou, Y: PS-TuP-2, **1**