Plasma Science and Technology
Room: 210B - Session PS+EM-MoA

Directed Self Assembly and Plasma Synthesis of Novel Materials
Moderator: Eric Joseph, IBM T.J. Watson Research Center

2:20pm **PS+EM-MoA1 Forward and Inverse Computational Tools for Directed Self-Assembly**, *G.H. Fredrickson, **Sean Paradiso***, University of California at Santa Barbara **INVITED**

This presentation will provide a tutorial on the physics of bulk block copolymer self-assembly, explaining how molecular parameters such as polymer architecture, composition, and molecular weight influence the size and symmetry of nanoscale domains. In thin films, additional variables such as surface and substrate interactions and substrate topology are important in "directing" the self-assembly and thereby achieving morphologies and features useful for pattern transfer in lithography. A powerful computational framework based on polymer field theory will be described that enables simulations to be conducted for a wide range of block copolymer formulations subject to arbitrary topological confinement ("grapho-epitaxy") or substrate chemical modulation ("chemo-epitaxy"). Our recent work at UCSB has involved computational studies of block copolymer directed self-assembly (DSA) in a variety of confining templates that can be produced using conventional lithography tools and targeting both line/space patterns and vertical interconnects (VIAs). The research aims to identify polymer architectures and compositions along with template geometries and surface treatments that lead to robust DSA structures. Beyond process windows for perfect structures, we have studied defect states and the free energy landscape connecting them to perfect states, thereby providing estimates of equilibrium defect populations and kinetic barriers for defect annealing. I will finish the presentation with an example of an "inverse design" calculation, namely the identification of a template and polymer composition that optimally produces a desired self-assembled pattern. Further developments in this area will be necessary for DSA to become a practical tool in next generation lithography.

3:00pm **PS+EM-MoA3 Improvement of Block Copolymer Masked Silicon Etch Profile using Neutral Beam**, ***Deokhyun Yun**, J.W. Park, H.S. Kim, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

These days, bottom-up block copolymer (BCP) lithography is widely investigated as alternative patterning method for deep nanoscale device replacing conventional top-down photolithography. The most widely used BCP material is polystyrene (PS)/polymethyl methacrylate (PMMA) and, nanoscale PS mask features formed on the substrates after the direct self-assembly are easily damaged by the plasma processing. Previously, neutral beam etching has been used to etch semiconducting materials without surface charging and damaging by using a highly directional radical beam instead of conventional plasma assisted ion beam. In this study, the nano-structured silicon was fabricated for nano-devices such as optical devices and transistor devices using BCP as the mask and the effect of Cl_2/Ar neutral beam instead of Cl_2/Ar ion beam on the etch characteristics of BCP and silicon was investigated. The use of neutral beam instead of ion beam decreased the degradation of BCP during the etching, therefore, more anisotropic silicon etch profile in addition to the improved etch selectivity of silicon over BCP could be observed. Also, by using the neutral beam instead of ion beam, the improvement of line edge roughness could be obtained.

3:20pm **PS+EM-MoA4 Plasma Etching of Directed Self Assembly based Patterns for Aggressively Scaled CMOS Applications**, ***Hiroyuki Miyazoe**, H. Tsai, R.L. Bruce, S.U. Engelmann, M. Brink, A. Pyzyna,* IBM T.J. Watson Research Center, *C. Liu,* IBM Albany Nanotech Center, *A. Vora, D. Sanders,* IBM Almaden Research Center, *M. Maher, W. Durand, C. Ellison, G. Willson,* The University of Texas at Austin, *M. Guillorn, E.A. Joseph*, IBM T.J. Watson Research Center

As the feature size in CMOS technology continues to shrink, patterning below 30 nm pitch faces many challenges. Directed self-assembly (DSA) [1] and sidewall image transfer (SIT) [2] patterning techniques can augment conventional lithographic patterning by providing sublithographic multiplication of feature pitch. Recently, our group successfully demonstrated the electrical characterization of FinFET devices comprising fins formed by DSA of poly (styrene-block-methyl methacrylate) (PS-b-PMMA) block copolymers (BCPs) at 28nm fin pitch [3]. In addition, we demonstrated copper lines with dielectric patterns formed by DSA at 28nm pitch followed by metallization [4]. Patterning of Si, SiNx and SiOx at a ~24 nm feature pitch using PS-b-PMMA BCP was also shown [3]. In this work, we discuss a parametric study of factors impacting fine feature patterning to further optimize DSA line-space patterning using PS-PMMA BCPs at 28 and 24nm pitch, and high chi BCP at 20nm and 18.7nm pitch. The use of templated DSA to generate line-space structures in the aforementioned materials was used to investigate the control of critical dimension (CD), line edge roughness (LER) and line width roughness throughout the patterning process. The line roughness of the hardmask becomes smaller at the lower substrate temperature during etch. The CD of lines was controlled well between 11nm and 15nm at 28nm pitch by controlling the etching time while keeping the LER constant (at ~3nm). We also confirmed that O_2-free plasma gas chemistry is more advantageous for BCP patterning in case of organic-organic polymer. These initial patterning studies may play an important role in understanding feature formation and density limiting ground rules.

[1] J. Cheng et al., SPIE 2010, [2] H. Yaegashi. SPIE 2012, [3] Tsai, IEDM 2014, [4] Pyzyna VLSI 2015

4:00pm **PS+EM-MoA6 Microplasma Based Synthesis of Nanomaterials**, ***Michael Gordon***, University of California at Santa Barbara **INVITED**

We present a hybrid plasma spray deposition technique, based on geometrically-confined, supersonic microplasma jets, which can create a wide range of metal, metal oxide/sulfide, and semiconductor nanoparticles and nanostructured thin film materials (e.g., CuO/CuS, ZnO, SnO_2, NiO/$NiFe_2O_4$) on virtually any surface. Organometallic or aerosolized precursors are broken down in a hollow cathode microplasma jet under different reducing/oxidizing atmospheres at high pressure (10-100 torr), creating a directed flux of active metal and oxide species for the subsequent growth of nanostructured films. Interaction of the jet afterglow with the background gas can create additional species (e.g., excited neutrals, radicals, etc.) which participate in film growth. By adjusting supersonic flow characteristics and plasma operating conditions, deposits ranging from isolated nanoparticles to films of fibers, aggregates, nanowires, and dense columns can be realized. The talk will highlight our recent efforts in nanomaterial synthesis via microplasmas with emphasis on the physics of the jet source, dynamics of the growth process, and applications such as solar cell electrodes, photo(electro)catalysis, and nanogranular films for magnetic exchange bias applications.

4:40pm **PS+EM-MoA8 Nucleation of Silicon Nanocrystals in a Remote Plasma without Subsequent Coaguation**, ***Ilker Dogan***, Eindhoven University of Technology, Netherlands, *S.L. Weeks, S. Agarwal,* Colorado School of Mines, *M.C.M. van de Sanden*, Dutch Institute for Fundamental Energy Research (DIFFER), Netherlands

We report on the growth mechanism of spherical silicon nanocrystals (Si-NCs) in a remote expanding Ar plasma using a time-modulated SiH_4 gas injection in the microsecond time range. Under identical time-modulation parameters, we varied the local density of the SiH_4 gas by changing its stagnation pressure on the injection line over the range 0.1-2.0 bar. We observed that nanocrystals were synthesized in a size range from 2 nm to 50 nm with monocrystalline morphology. Smaller nanocrystals (2-6 nm) with narrower size distributions and with higher number densities were synthesized with an increase of the SiH_4 gas-phase density. We related this observation to the rapid depletion of the number density of the molecules, ions and radicals in the plasma during nanocrystal growth, which can primarily occur via nucleation with no significant subsequent coagulation. In addition, in our remote plasma environment, rapid cooling of the gas in the particle growth zone from 1500 K to 400 K significantly reduces the coalescence rate of the nanoparticles, which makes the coagulation process highly unlikely. Our observations on nanocrystal formation via nucleation indicated that subsequent coagulation for further growth is not always an essential step on nanoparticle formation.

5:00pm **PS+EM-MoA9 Atmospheric Plasma Synthesis of Metallic Platinum Nanoparticles for PEMFC Technology using an Organometallic-Carbon Solution Nebulized in the Post-Discharge of an RF Torch**, ***Joffrey Baneton**, D. Merche,* ULB, Belgium, *M. Raes,* VUB, Belgium, *V. Debaille,* ULB, Belgium, *G. Caldarella, V. Stergiopoulos,* ULg, Belgium, *H. Terryn,* VUB, Belgium, *N. Job,* ULg, Belgium, *F.A.B. Reniers*, ULB, Belgium

Catalytic layers are one of the most important components of proton exchange membrane fuel cells (PEMFC) because they directly influence the transport of matter and the reactivity of the electrodes [1]. In many cases, platinum associated with carbon black forms the most interesting material because of its very high catalytic activity [2]. Unfortunately, some limitations remain due to the cost of platinum and the difficulty to control the structure of the carbon support.

In this study, we propose a new promising technique using platinum (II) acetylacetonate [Pt(acac)$_2$] powder mixed with porous carbon and nebulized in a RF atmospheric plasma torch directly on commercial gas diffusion layer (GDL). This fast and "one-pot" methodology leads to the formation of homogeneous and reproducible samples with a variable and controlled content of metallic platinum on the surface, as analyzed by X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM). The catalytic activity per mass unit can be studied by a combination of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and electrochemical measurements.

We demonstrate that the plasma treatment and mostly the reactive oxygen species play a critical role in the activation of the support surface and the binding of the platinum nanoparticles on it, reinforcing previous observations [3,4]. In the case of an argon-oxygen plasma pretreatment of the GDL, a significant increase of the platinum content on the surface can be observed.

The influence of different process parameters on the synthesis of the platinum nanoparticles was studied. We show that the carrier gas flow rate, the power injected in the discharge and the treatment time do not have a significant impact on the surface composition. On the other hand, some nebulizer parameters such as the number of pulses or the loading of Pt-C allow the tuning of the amount of Pt grafted on the surface without altering its metallic nature.

Finally, the influence of the type of carbon powder (e.g. CB, CX or CNTs) was investigated. It appears that it can modify the surface organization and consequently also the intrinsic characteristics of the material. It reveals that the distribution of platinum nanoparticles and the access to the catalytic sites can be optimized depending of the porosity and the active surface of the carbon support.

[1] Gasteiger et al. Handbook of Fuel Cells – Fundamentals, Technology and Applications. **2003**, 3, 593

[2] Chatenet et al. New and Future Developments in Catalysis. **2013**, 401-423

[3] Pireaux et al. Method for Depositing Nanoparticles on Substrates, **2002** (Patent)

[4] Claessens et al. *Nanotechnology*, **2010**, 21, 38, 385603

5:20pm **PS+EM-MoA10 Low Energy Helium Ion Irradiation Induced Surface Modification of Metals**, ***Irem Tanyeli****, FOM Institute DIFFER, Netherlands, *L. Marot, D. Mathys,* University of Basel, Switzerland, *M.C.M. van de Sanden,* FOM Institute DIFFER, Netherlands, *G. De Temmerman*, ITER Organization

Many applications, such as energy harvesting, energy storage, optoelectronics, demand nanomaterials and/or nanostructured surfaces for an enhanced activity. Various techniques, which can be grouped under top-down and bottom-up approaches, exist and are worked on by many researchers in order to fulfill the demands of these applications. There are some critical requirements that needs to be satisfied by nanostructures before being implemented in any application, such as high porosity, good contact between different crystallites and good electrical conductivity. Standard nanostructuring approaches, such as wet-chemical processing, can give very homogeneous particle sizes, but the contact between the particles is often poor and a necking treatment is needed to alleviate this limitation. In this study, Helium ion induced nanostructuring is proposed as an efficient technique. This top-down approach provides a good control over morphology, high porosity, good conductivity and it enables post processing, such as oxidation and nitridation.

Metal surfaces are exposed to pure Helium plasma under extreme ion flux (in the range of 10^{23} m^{-2}s^{-1}) and low ion energy (< 100 eV) conditions at Pilot-PSI, linear plasma generator. Different surface modifications on various metals, such as iron, titanium, copper and aluminum, are observed.[1] Pillar like structures are formed on copper and aluminum surfaces, whereas fiber like nanostructures are observed on iron surface. Controlled nanostructure formation on tungsten and molybdenum surfaces has been reported.[2] Consistently, nanostructure formation on iron surface has been controlled with surface temperature and ion fluence in this study.[3] It has been known that metal oxides are good candidates to be used as photoelectrodes in photoelectrochemical cells. WO$_3$ and α-Fe$_2$O$_3$ are two of the most widely studied photoanodes. Hence, Helium ion induced tungsten and iron nanostructured surfaces are oxidized to the desired phases to be tested in photoelectrochemical cells. 1mA/cm^2 of photocurrent density for WO$_3$ has been achieved.[4]

[1] **I. Tanyeli**, L. Marot, D. Mathys, M. C. M. van de Sanden, G. De Temmerman, Sci. Rep. 5:9779-8, 2015.

[2] G. De Temmerman et al., J. Vac. Sci. Technol. A, 30, 041306-6, 2012.

[3] **I. Tanyeli**, L. Marot, M. C. M. van de Sanden, G. De Temmerman, ACS Applied Materials & Interfaces 6 (5), pp 3462-3468, 2014.

[4] M. de Respinis, G. De Temmerman, **I. Tanyeli**, M. C. M. van de Sanden, R. P. Doerner, M. J. Baldwin, R. van de Krol , ACS Applied Materials & Interfaces 5 (15), pp 7621-7625, 2013.

*** Coburn & Winters Student Award Finalist**

Authors Index

Bold page numbers indicate the presenter