

## Plasma Science and Technology Division Room 104A - Session PS+EM+NS+SS-TuA

### Plasma Processing of Challenging Materials - II

**Moderators:** Michael Gordon, University of California at Santa Barbara, Wei Tian, Applied Materials Inc.

#### 2:20pm PS+EM+NS+SS-TuA-1 Self-limiting Growth of III-nitride Materials via Hollow-cathode Plasma-ALD: Structural and Chemical Analysis, *Necmi Biyikli, A Mohammad, D Shukla*, University of Connecticut **INVITED**

Plasma-assisted/enhanced atomic layer deposition (PALD) provides an alternative route for the low-temperature synthesis of III-nitride thin films with sub-monolayer precision thickness control, ultimate three-dimensional conformality, and large-area uniformity. On the other hand, PALD synthesis of AlN, GaN, and InN films required relatively long plasma co-reactant exposure durations (40 - 120 sec) to achieve self-limiting surface saturation with minimal carbon impurities which directly correlates the effectiveness of the ligand-removal process. During such extensive plasma half-cycles, the plasma source itself is exposed to elevated temperatures and along with energetic hydrogen radicals, which resulted in etching of conventional quartz-based inductively coupled plasma (ICP) sources. We have mitigated this problem by using a stainless-steel based capacitively-coupled hollow-cathode plasma (HCP) source, which reduced the oxygen impurity levels at least two orders of magnitude in GaN films while increasing the average film grain/crystallite size of AlN films by one order of magnitude.

Using HCP-assisted ALD (HCP-ALD), we have grown the entire III-nitride wide bandgap semiconductor family (AlN, GaN, InN) at  $\leq 200^\circ\text{C}$  substrate temperatures with single-phase hexagonal poly-crystalline material quality. However, there is still plenty of room and need for improvement in material properties before we can use these layers as active device layers. A careful systematic study needs to be carried out to achieve device quality III-nitride films via HCP-ALD. In this talk, we will present an overview of our HCP-ALD efforts including our recent materials characterization results obtained with a custom-design HCP-ALD reactor. A particular focus will be devoted to the structural and chemical properties of the III-nitride films and how they correlate with reactor parameters and plasma conditions.

#### 3:00pm PS+EM+NS+SS-TuA-3 Electrostatic Charge of Solution-droplet in Plasma-coupled Micro Reactor, *Tae Hwan Kim, S Lee*, National Fusion Research Institute, Republic of Korea

Plasma-liquid interaction research has increased because of emerging technological applications such as material synthesis, plasma bio-applications, environmental applications, and agriculture/food applications. Recently, an important scientific breakthrough in the understanding of the liquid reaction at the plasma-liquid interface that an electron transfer reaction at the plasma-liquid interface that leads to electrochemical reactions, which is referred to as the plasma electrochemical reaction [1]. Further evidence of plasma electron reaction (PER) was observed that the electrons in plasma can be solvated in a plasma electrochemical system [2].

In this talk, we present a new reaction pathway in which plasma-liquid interaction can cause an electrostatic charge in a liquid and the electrostatically charged solution can produce an electrochemical reaction. The experiments were performed with our newly designed plasma-coupled-microreactor (PCM), which can control the ambient gas and initiate a rapid plasma electrochemical reaction. Helium(He)-droplets and liquid-droplets were formed, and microplasma-droplets were ignited by dielectric barrier discharge (DBD). The generated microplasma-droplet can induce not only PER but also an electrostatic charge in a solution. The charge of the solution by microplasma-droplet and liquid-droplet interaction can be affected by the type and amount of stabilizer, the acidity of the solution, and the length of the electrodes used to form microplasma-droplets.

[1] C. Richmonds, M. Witzke, B. Bartling, S. W. Lee, J. Wainright, C. Liu, R. Mohan Sankaran, Electron-Transfer Reactions at the Plasma-Liquid Interface. *J. Am. Chem. Soc.* 133, 17582-17585 (2011)

[2] P. Rumbach, David M. Bartels, R. Mohan Sankaran, David B. Go, The solvation of electrons by an atmospheric-pressure plasma. *Nat. Commun.* 6, 7248 (2015).

#### 3:20pm PS+EM+NS+SS-TuA-4 Surfactant-free and Stable Colloidal Metal Oxide Ultra-small Quantum Dots via Plasma-liquid Electrochemistry, *Dillibabu Padmanaban, D Carolan, R McGlynn, T Velusamy, P Maguire, D Mariotti*, Nanotechnology & Integrated Bio-Engineering Centre, Ulster University, UK

Metal oxides are materials of great importance and interest with exceptional chemical stability, tunable optical and electrical properties and, importantly, meeting cost and environmental requirements for a sustainable future. For these reasons metal oxides nanoparticles are being investigated for a very wide range of applications that include energy harvesting and solar conversion and for exploiting nanoscale effects. However, due to synthesis challenges, the properties of ultra-small and quantum confined metal oxide nanoparticles, or quantum dots (QDs), are still very little understood while expected to offer exciting opportunities. Here we demonstrate that the synthesis of metal oxide QDs can be achieved by plasma-liquid electrochemistry with exceptional control of the size distribution even for particles well below 2 nm in diameter. Plasma-induced chemistry initiated at the plasma-liquid interface allows for rapid and simple production of highly stable colloidal suspension in ethanol of surfactant free metal oxide QDs, where a solid metal foil acts as the metal precursor. We provide an overview of these capabilities for a range of metal oxides that include Cu, Ni, Co, Mo and Zn oxides. We then study in detail the synthesis mechanisms leading to cupric oxide (CuO) QDs providing a range of experimental evidence that clarifies chemical reaction pathways due to the plasma interacting with ethanol. For a better understanding of the plasma chemistry, the process was also studied with different electrodes so to assess the impact of QDs formation in the overall plasma-ethanol chemistry. We have carried out extensive material characterization for the QDs and we have also analysed liquid products at different conditions by Fourier transform infrared spectroscopy, ultraviolet-visible spectroscopy, nuclear magnetic resonance, mass-spectroscopy etc. Our work points at the role of different species in the synthesis of QDs. We believe that some of these chemical pathways may be general and applicable to the formation of other metal oxide QDs, however in some cases (e.g. for Mo-oxide) we expect some deviations. Overall our work discloses important general aspects of plasma-liquid interactions, in particular when ethanol is used. The study of the properties of our metal-oxide QDs uncovers quantum confinement effects that can become particularly useful in many application and suggest exciting opportunities in the control of defects and achieving phases that are difficult to produce with other methods.

#### 4:20pm PS+EM+NS+SS-TuA-7 From Organometallic Precursors to Bimetallic Nanocatalysts using Atmospheric-pressure Plasma Processes, *Joffrey Baneton, J Mertens, M Smiljanic, S Cauchies, T Segato*, Université Libre de Bruxelles, Belgium; *Y Busby*, Université de Namur, Belgium; *G Caldarella*, Université de Liège, Belgium; *V Debaille, S Godet*, Université Libre de Bruxelles, Belgium; *J Pireaux*, Université de Namur, Belgium; *N Job*, Université de Liège, Belgium; *M Gordon*, University of California at Santa Barbara; *M Sankaran*, Case Western Reserve University; *F Reniers*, Université Libre de Bruxelles, Belgium

Developing new technologies to produce energy while respecting the environment is one of the important challenges in materials science. One of the possible routes is the use of hydrogen fuel cells. Unfortunately, some limitations remain such as the electrocatalysis of the reduction of dioxygen which requires a rare and expensive metal: platinum [1]. Therefore, minimizing its amount at the cathode while maximizing its accessibility, electroactivity and stability constitutes one of the main goal of current research. An interesting way consists in the synthesis of platinum-based alloys. Indeed, it is well known in the literature that combining two metals leads to the production of durable materials with higher activity [2].

Different routes can lead to the formation of bimetallic nanostructures including wet-chemistry, ultrasound processes or thermal evaporation. In this catalogue of methods, atmospheric-pressure plasma techniques are very attractive due to their versatility, rapidity and ease of use. In the present research, two different kinds of reactors, a microplasma device [3] and radio-frequency plasma torch [4], have been used to study the synthesis of bimetallic nanoparticles from acetylacetonate precursors. A complete chemical and morphological characterization is provided thanks to the combined use of X-ray photoelectron spectroscopy, transmission electron microscopy, UV-visible spectroscopy and X-ray crystallography.

Different experimental parameters can play a crucial role in the reduction process of the organometallic precursors. For example, concerning the microplasma system, the initial concentrations have a direct influence on

the size distribution and agglomeration while, concerning the RF plasma torch treatment, the nature of the plasma gas mixture can limit the production of nanoparticles or favor their anchoring at the surface of a carbon support [5]. After optimization of the processes, electrochemical measurements were conducted to evaluate their activity, stability and performances as catalysts for hydrogen fuel cells.

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[1] F. Maillard et al. In: Carbon materials for catalysis (2009), 429-480.

[2] Z. Li et al. Int. J. of Hydrogen Energy (2012), 37, 14152–14160.

[3] C. De Vos et al. J. Phys. D: Appl. Phys. (2017), 50, 105206.

[4] D. Merche et al. Plasma Process. Polym. (2016), 13, 91–104.

[5] A. Felten et al. J. Phys. D: Appl. Phys. (2007), 40, 7379.

**4:40pm PS+EM+NS+SS-TuA-8 Synthesis of Hydrogenated Amorphous Carbon Nanoparticles using High-Pressure CH<sub>4</sub>+Ar Plasmas and Their Deposition, Kazunori Koga, S Hwang, K Kamataki, N Itagaki, Kyushu University, Japan; T Nakatani, Okayama University of Science, Japan; M Shiratani, Kyushu University, Japan**

Nanostructure fabrication such as nanoparticles through bottom-up processes is important in nanotechnologies due to their size-related properties [1]. Plasma is a powerful tool to produce nanoparticles. To control their size, pulsed discharge plasmas are commonly employed, but the plasmas have the limitation of the throughput. To realize continuous production, we have developed a multi-hollow discharge plasma chemical vapor deposition (MHDPCVD) method. We have succeeded in producing crystalline Si nanoparticles of 2 nm in size using hydrogen diluted silane plasmas [2, 3]. Here we applied the method to synthesis carbon nanoparticles. The experiments are carried out by CH<sub>4</sub>+Ar MHDPCVD. CH<sub>4</sub> and Ar were injected into the reactor, flowed through hollows of 5 mm in diameter in the electrode. The gas flow rate ratio of CH<sub>4</sub> and Ar was 1:6. The total gas flow rate was 10 to 200 sccm. The pressure was kept at 2 Torr. Discharges were generated in hollows by applying rf power of 40 W at 13.56 MHz. Nanoparticles are nucleated and grow in the discharges. They are transported outside of the discharges by the fast gas flow and the growth of the nanoparticles are stopped. They deposited on TEM mesh grids set on the substrate holder 50 mm far from the electrode. From TEM measurements, spherical nanoparticles were deposited on the grid. The mean size decreases from 270 nm for 10 sccm to 20 nm for 120 sccm. The gas residence time for 120 sccm is 1/12 of that for 10 sccm. The size for 120 sccm is 1/13.5 of that for 10 sccm. The results indicate that the size of carbon nanoparticles are controlled by gas residence time of nanoparticles in plasmas. Above 125 sccm, No nanoparticle is observed on the TEM mesh. It suggests that deposition of nanoparticles depends on gas flow velocity and direction on the substrate.

[1] M. Shiratani, et al., J. Phys. D 44 (2011) 174038.

[2] T. Kakeya, et al., Thin Solid Films 506 (2006) 288.

[3] K. Koga et al., ECS Transactions 77 (2017) 17.

**5:00pm PS+EM+NS+SS-TuA-9 Antimony-doped Tin Oxide Nanocrystals Synthesized by Low Temperature Plasma, Qinyi Chen, E Thimsen, Washington University in St. Louis**

For electrochemical applications, metal-oxide materials are attractive as electrodes for reactions occurring at positive potentials in the presence of water. Often, these metal-oxide materials function as an electrically-conductive support for a noble metal catalyst, and therefore must have very high specific surface area. Among conductive metal-oxide materials, antimony-doped tin oxide (ATO) stands out with its combination of: 1) high chemical stability over a wide range of pH values and reduction potentials, 2) high electrical conductivity, and 3) abundant constituent elements. Synthesis of ATO nanocrystals has been developed in liquid phase using sol-gel and colloidal methods. However, post-synthesis heat treatments are required to activate the electron donors and increase the conductivity of ATO nanocrystal assemblies prepared using liquid-phase techniques, which may adversely affect the surface area and pore structure of the material. In this work, we report on our efforts to synthesize monodispersed, conductive ATO nanocrystals through a single-step low temperature plasma growth method without any post treatments. Precursor vapors of tin and antimony were fed into a radiofrequency, flow-through low temperature plasma reactor. The precursor vapors reacted to nucleate ATO nanocrystals. Thin films comprised of ATO nanocrystals were then immediately deposited by supersonic impact deposition of the aerosol resulting from plasma synthesis. The resulting materials were characterized

by a variety of methods to determine film thickness, porosity, nanocrystal size, and elemental composition. Local electron concentration and mobility within the nanocrystals were assessed by Fourier-transform infrared absorption spectroscopy. Hall effect was used to characterize longitudinal electrical transport in the film. The nanocrystal growth mechanism in the plasma will be discussed with a focus on antimony dopant incorporation. The effects of nanocrystal size on the transport properties of ATO thin films will be presented.

**5:20pm PS+EM+NS+SS-TuA-10 Femtosecond Laser Texturing of Plasma-immersed Ti to Create TiN, Chisung Ahn, E Barlaz, D Ruzic, University of Illinois at Urbana-Champaign**

Pulsed femtosecond lasers have been used as a functionalization method for metal surfaces due to their ability to produce nanostructures uniformly with easily controlled user inputs such as spot size and exposure repetition. Laser assisted nitriding of Ti in ambient nitrogen has previously been demonstrated in our group to significantly reduce native oxides. A major challenge to the current process is the limited ability of the laser to produce nitrogen radicals.

In this study, we investigate the effects of increased nitrogen radical concentration on surface topography and chemical composition for textured Ti metal. A secondary DC plasma is generated along the path length of the laser close to the sample surface in ambient nitrogen and under vacuum. The surface topography and chemical compositions of the resultant Ti coupons are analyzed by SEM and XPS respectively. Changes to hydrophilicity are quantified using contact angle measurements.

**5:40pm PS+EM+NS+SS-TuA-11 Modeling Chemical Reactions in Contact Glow Discharge Electrolysis, Bocong Zheng, M Shrestha, K Wang, T Schuelke, Q Fan, Michigan State University**

Contact glow discharge electrolysis is becoming attractive for nanomaterials manufacturing and surface engineering. In this discharge electrolysis, an electrode is submerged in a liquid electrolyte and a plasma is formed in a vapor layer around the electrode. The process combines the characteristics of electrolysis and plasma discharges, creating high-energy-density plasmas that lead to intensive physical processes and chemical reactions on the working electrode. The authors have found that the physical processes and the chemical reactions could be decoupled under certain conditions. In that case, a textured electrode surface could be created through a chemical-reaction-dominated process instead of an irregular porous surface produced by the physical-reaction-dominated interactions. The mechanisms are not clearly understood yet. This study aims to elucidate the plasma characteristics and the chemical reactions in contact glow plasma electrolysis. A plasma fluid model is established to predict the discharge process with constraint conditions obtained from the experiments. The modeling reveals that the plasma is highly electronegative, and the dominant neutral species are H<sub>2</sub> and O<sub>2</sub> dissociated from water vapor. The formation of textured surface is attributed to the anisotropic chemical etching by the reactive species generated in the plasmas.

**6:00pm PS+EM+NS+SS-TuA-12 Effects of Light Ion Beam Irradiation in Plasma Etching Processes, Kazuhiro Karahashi, T Ito, H Li, M Isobe, K Mizotani, S Shigeno, Osaka University, Japan; M Fukasawa, A Hirata, T Tatsumi, Sony Semiconductor Solutions Corporation, Japan; S Hamaguch, Osaka University, Japan**

Gases containing hydrogen are widely used in microfabrication processes of electronic devices using plasma etching. For example, HBr gas is used for silicon etching, hydrofluorocarbon gases are used for silicon oxide etching, and Hydrocarbon-based non-corrosive gases are used for transparent conducting oxides etching. Unlike other atoms, hydrogen is lighter in weight, smaller in atomic radius, and chemically reactive, so it has various effects in the etching process. In order to precisely control the etching reaction and realize nanometer order microfabrication processes, it is necessary to clarify the effect of hydrogen. In this study, by comparing various effects on etching processes between hydrogen and helium incident ions using molecular dynamics (MD) simulation and ion beam experiments, physical and chemical effects by such light ion injection on etching processes were evaluated.

We have shown in this study based on MD simulation and ion beam experiments that, when a Si surface exposed to an O radical flux is simultaneously irradiated by an H<sup>+</sup> or He<sup>+</sup> ion beam, diffusion of oxygen atoms into the Si film is promoted. Since the enhanced diffusion occurs in a similar manner in both cases of H<sup>+</sup> and He<sup>+</sup> ion injections, it is clear that the enhanced diffusion is essentially caused by knock-on effects by incident

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light ions. On the other hand, in the case of etching of ZnO, which is an ionic crystal, our beam experiments have shown that its crystal size decreases by light ion irradiation using in-plane X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM) measurements. The reduction of grain sizes seems correlated with the reduction of the physical sputtering yield of the ZnO film.

The results above show the following two physical effects by irradiation of a substrate with light ions such as  $H^+$  and  $He^+$  ;1) enhancement of diffusion of heavy atoms deposited on the substrate surface into it's the bulk of the film and 2) decrease of grain sized of ionic crystalline substrate due to amorphization and recrystallization. The decrease of grain sizes, which induce the increase in grain boundary areas may contribute to an increase in sputtering yield of the substrate.

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