

Plasma Science and Technology

Room 124 - Session PS2-MoA

Plasma Chemistry and Catalysis I

Moderators: Michael Gordon, University of California at Santa Barbara, Mohan Sankaran, University of Illinois at Urbana-Champaign

4:00pm **PS2-MoA-11 Stress Reduction of Hydrogenated Amorphous Carbon Films by Controlling Incorporation of Carbon Nanoparticles, Kazunori Koga, S. Ono, T. Okumura, K. Kamataki, M. Shiratani, Kyushu University, Japan** **INVITED**

Stress reduction of hydrogenated amorphous carbon (a-C:H) films has been an important topic in improving the performance of the protective coating, which has been employed for the masking of dry etching, automotive parts, and electrodes of batteries [1,2]. Metal nanoparticle incorporation into the films has been one conventional method to reduce stress [3,4]. However, it led to metal contamination of the films, resulting in the deterioration of the semiconductor device performance. In this study, inspired by the insertion of the metal nanoparticles, we aimed to relieve the stress by incorporating the carbon nanoparticles (CNPs) into the a-C:H films. As the first step, we have successfully controlled the size of nanoparticles by plasma chemical vapor deposition (CVD) [5,6]. Then, we succeeded in controlling the coverage of carbon nanoparticles (CNPs) deposited on substrates using capacitively coupled plasma chemical vapor deposition (CVD), which has been widely employed in large-area deposition. From TEM images, deposited CNPs were classified into two size groups. The mean size of the smaller CNP group is around 5 nm, and that of the larger CNP group is around 25 nm. We succeeded in controlling the coverage C_p of CNPs with discharge duration without unexpected agglomeration. Based on the results, we fabricated a-C:H/CNP/a-C:H sandwich-like films using the parallel plate plasma CVD reactor. Ar and CH₄ mixture gas was introduced from the top of chamber at 19 sccm and 2.6 sccm, respectively. The total pressure was kept at 0.3 Torr. The gas flow rate and the pressure were same as those for the CNP deposition. The mass density of deposited a-C:H films is 1.88 g/cm³. The dependence of the film stress on the C_p . With increasing the C_p , the stress decreases from 1.59 GPa at $C_p = 0\%$ to 1.02 GPa at $C_p = 8.9\%$. It shows same value for $C_p = 15.9\%$. The reduction rate is 35.8%. On the other hand, the films' thickness and refractive index were kept at approximately 320 nm and 2 regardless of the C_p . The results indicate that a small amount of CNP incorporation can reduce the film stress.

[1] N. Hiwasa, et al., Jpn. J. Appl. Phys. Express 15, 106002 (2022). [2] C. Y. Ho, et al., Thin Solid Films 518(21), pp.6076-6079 (2010). [3] M. Constantinou, et al., Nanomaterials 8(4), pp.209-229 (2018). [4] R. Paul, et al., Appl. Surf. Sci. 257(24), pp.10451-10458 (2011). [5] S. H. Hwang, et al., Diam. Relat. Mater. 109, 108050 (2020). [6] S. H. Hwang, et al., Plasma and Fusion Research: Regular Articles 14, 4406115 (2019).

4:30pm **PS2-MoA-13 Is Plasma Electrochemistry Just Electrochemistry at Plasma-Liquid Interfaces? Learnings from Organic Reactions, Casey Bloomquist, E. Aydil, M. Modestino, New York University**

In plasma electrochemical synthesis, one of the electrodes of a traditional electrochemical cell is replaced by plasma. Recent work has focused on using plasma-generated solvated electrons to perform reductive chemistry in aqueous solutions. In this study, we explored the use of plasma electrochemistry for the largest industrial organic electrosynthesis process, the electrohydrodimerization of acrylonitrile (AN) to adiponitrile (ADN), a precursor to Nylon 6,6. We used a DC pin-to-liquid Ar plasma to study both negative polarity and positive polarity plasma interactions with aqueous AN. Interestingly, we did not produce ADN, which was expected to be created through radical coupling in a negative polarity plasma. However, we did produce H₂, H₂O₂, propionitrile (PN), O₂, CO₂, C₂, and C₃ hydrocarbons and AN-derived polymers with amounts depending on the AN concentration, current, and polarity. H₂ was produced in amounts 10 – 20 times that expected from Faradaic currents, highlighting the importance of non-electrochemical reactions. PN, a competing reaction in traditional ADN electrosynthesis, was produced at rates commensurate with Faradaic currents under negative potentials. However, under positive potentials, PN production was much higher than predicted by Faradaic currents, suggesting that PN production under either polarity may be produced via non-electrochemical pathways. Clearly, there is more to plasma electrochemistry than just electrochemistry.

4:45pm **PS2-MoA-14 Nonequilibrium Plasma Aerotaxy of In_xGa_{1-x}N Nanocrystals, Dillon Moher, E. Thimsen, Washington University in St. Louis**

Semiconductors with good stability in harsh chemical environments, tunable band gap, and non-toxicity are sought after for solar energy conversion and solid-state light sources. The solid solution of InN and GaN (In_xGa_{1-x}N) is a good candidate material whose band gap depends on the mole fraction of InN in the GaN (x). Full control over the composition can provide photon absorption and emission from the ultraviolet to the infrared. However, homogeneous thin film In_xGa_{1-x}N with intermediate x is plagued by strain-induced threading dislocations and phase segregation due to the miscibility gap. High material quality and tunability may be achieved in freestanding In_xGa_{1-x}N nanocrystals, absent of epitaxial growth and having distinct mixing behavior due to nanoscale effects. Moreover, nanocrystals may have 3D quantum confinement effects, high specific surface area, and compatibility with solution processing. Yet, their synthesis is underdeveloped. In this work, the synthesis of In_xGa_{1-x}N nanocrystals by nonequilibrium plasma aerotaxy was demonstrated. STEM-EDS observation showed that individual nanocrystals consisted of a mixture of InN and GaN. The nanocrystals, deposited into thin films, had a composition-dependent band gap demonstrated by UV-Vis extinction spectroscopy. Annealing procedures were pursued to improve the crystallinity and photoluminescence of the nanocrystal films. Decomposition of the nanocrystals, which occurred at temperatures of 600 °C and above, was suppressed when the nanocrystals were first coated with Al₂O₃ deposited by atomic layer deposition. Furthermore, the photoluminescence of the nanocrystals increased by an order of magnitude. This new synthesis strategy for In_xGa_{1-x}N nanocrystals is a step towards advanced optoelectronic applications, paving the way for further research into material property optimization and integration into devices.

5:00pm **PS2-MoA-15 Plasma-Based Reforming of LNG?, N. Lim, Michael Gordon, UC Santa Barbara**

Developing novel reacting systems for more sustainable use of our natural resources is central to both reducing the risks associated with CO₂ emissions and making the long-term transition to a more circular, sustainable, and electrified economy. Moreover, developing technologies to leverage and reform the energy density of global commodities such as liquefied natural gas (LNG), to produce clean H₂, olefins, and solid carbon without producing CO₂, could be game changing. Toward this end, we have been exploring how plasmas might be directly excited in liquid methane at cryogenic conditions to create value-added products.

This talk will highlight our preliminary work on striking and sustaining low (60 Hz) and high (~20 kHz) frequency, as well as pulsed, plasma discharges directly in liquid methane at ~100K (**Figure 1**), with emphasis on (i) the reactor configuration (i.e., with rotating electrodes to prevent carbon buildup), (ii) yield of H₂ and other (solid) hydrocarbon products, (iii) energy efficiency, and (iv) management and characterization (SEM/TEM) of the solid carbon product (**Figure 2**). Although the four-phase reaction environment encountered at cryogenic conditions – namely, plasma, gaseous H₂, slurry of frozen C₂₊ hydrocarbons, and solid carbon – presents many challenges, it is still possible to generate H₂, some C₂ olefins, and a graphite-like carbon product.

Various aspects of this unorthodox cryogenic reaction environment will be discussed including: what might be going on in the discharge?, is the plasma thermal or nonthermal?, does the input energy vaporize the methane?, how can the carbon be managed?, what products are formed under different plasma conditions?, what is the H₂ production rate and SER?, and might this process be a better or more useful way to re-gasify and reform LNG?

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