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 Cp 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 Cp. With increasing the Cp, the stress decreases from 1.59 GPa at Cp= 0 % to 1.02 GPa at Cp= 8.9 %. It shows same value for Cp= 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 Cp. 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 produceH_2, H_2O_2, propionitrile (PN), O_2, CO_2, C_2, and C_3 hydrocarbons and AN-derived polymers with amounts depending on the AN concentration, current, and polarity. H_2 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***, D. Moher, **Elijah 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 Al_2O_3 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 CO_2 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 liquified natural gas (LNG), to produce clean H_2, olefins, and solid carbon without producing CO_2, 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 H_2 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 H_2, slurry of frozen C_2+ hydrocarbons, and solid carbon - presents many challenges, it is still possible to generate H_2, some C_2 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 H_2 production rate and SER?, and might this process be a better or more useful way to re-gasify and reform LNG?

5:15pm **PS2-MoA-16 Hydrogen Production from Nebulized Ethanol in a Nanosecond Pulsed Discharge***, **Linus Nyssen**, T. Fontaine, D. Petitjean,* Université libre de Bruxelles, Belgium*; N. De Geyter,* Ghent University, Belgium*; F. Reniers,* Université libre de Bruxelles, Belgium

Means of energy production that don't emit greenhouse gases (GHG) are highly sought after. H_2 is a great candidate, as it could serve as fuel as well as energy storage for intermittent sources. For certain industrial sectors such as the steel industry, it is often the only viable alternative mentioned. Today H_2 is mainly produced by the Steam Methane Reforming process, emitting GHG in the process. The only alternative at the moment is water electrolysis but is highly demanding in energy: $\Delta_r H° = 285.83\ kJ/mol_{H2}$.

We investigate other sources to produce H_2 through plasma reforming. As an alternative to gas feedstocks in a plasma discharge, we use liquids such as ethanol, because it yields a high H/C ratio while staying liquid at room temperature. By spraying this ethanol inside an Ar discharge, we produce a high contact surface between the plasma and liquid phase compared to plasmas at the surface of a liquid. While aerosols in a plasma discharge are more often used for film deposition, we investigate the use of the method at atmospheric pressure for liquid conversion to H_2. To ignite the discharge, a nanosecond pulsed plasma is used, yielding high electric fields and allowing for high energy reactions while keeping the reactor at room temperature.

In this work, the conversion of ethanol to H_2 is investigated while varying parameters such as the pulse width, the voltage and the gap between electrodes and establishing their influence. We monitor conversion, selectivity and consumed power to extract the energy cost to produce H_2. The pin-to-rod reactor used has 6 pins at high voltage surrounding a central rod at ground potential. This conformation makes for a plasma section through which the gas and aerosols flow perpendicularly. The pulses are triggered 4000 times a second, so that each pulse is triggered in a new batch of gas & liquid, given the flow. Pulse widths of 50, 250 and 450 ns are used, at gaps of 2 and 6 mm, while using 10, 14 and 18 kV to trigger the discharge, giving a pulse energy ranging from 0.25 – 1.00 mJ/pulse. The conversion ranges from 3.96 to 21.01 % with the best conversion obtained at an energy of 1.00 mJ/pulse (obtained at 450 ns), yielding an energy cost of 287.65 kJ/mol H_2. For all conditions, the highest conversions and pulse energy were obtained for the larger gap. Interestingly, the selectivity for CO rises significantly (3.33 % to 7.60 % on average) when the gap is larger. These first results suggest an efficient way of producing H_2 at an interesting energy cost.

Author Index

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