Tuesday Afternoon, December 13, 2022

Plasma Processing
Room Naupaka Salon 1-3 - Session PS-TuP
Plasma Processing Poster Session

PS-TuP-1 Flexible Atmospheric Pressure Plasma Jet Device with Built-in Electrodes for Operation in Wet Environments*, Jae Young Kim*, *G. Bae, E. Jung, H. Tae,* Kyungpook National University, Republic of Korea

The AP-plasma jet (APPJ) device, which can realize nonthermal AP-plasma with a simple configuration of an electrode and a conduit, ignites the discharge gas flowing through the conduit by a powered electrode, and delivers the plasma plume to the outside of the conduit. In order to effectively utilize the APPJ for material processing, various efforts have been tried to transfer the plasma and its by-products as close to the target as possible. For this purpose, there are several reports of fabricating APPJ devices using flexible conduits such as plastic tubes instead of glass or ceramic conduits [1,2].

In this study, we describe a new flexible atmospheric pressure plasma jet (APPJ) device made of hollow-core optical fibers and introduce two potential applications: endoscopic plasma treatment and de-composition of aqueous phosphorus compounds. A long and highly flexible micro-plasma jet device made of three hollow-core optical fibers has been proposed for use in humid environment. In spite of a small inner diameter and a low gas flow rate of the APPJ device, the generated plasma plume is stable and capable of treating small target materials. In the proposed APPJ device, the wire electrode is completely isolated inside the hollow inside of the optical fiber, so there is no contact with the environment at the end of the device from which the plasma plume is emitted. This feature allows the device to operate both safely and reliably in humid environment or even under water.

The proposed long flexible APPJ device is ideal for endoscopic surgery due to the plasma characteristics and stability in environments with significant amounts of moisture. The exceptional flexibility and length of the device will enable it to reach diverse areas inside the human body with a biopsy channel of endoscopes. This work enables directed therapeutic methods based on a flexible APPJ device and presents AP-plasma endoscopy as a new physical therapeutic method. As another potential application, we also demonstrate that the proposed APPJ device can be used to decompose phosphorus compounds in water into their phosphate form. The preliminary works on the decomposition of phosphorus compounds show that the decomposition method by in-liquid plasma can be directly used as a promising pretreatment process for the ascorbic acid method to determine total phosphorus in fresh water.

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PS-TuP-2 Enhanced Hydrogen Production from the Cracking of Waste Hydrocarbons Using Liquid-Phase Plasma*, Kyong-Hwan Chung,* Sunchon National University, Republic of Korea*; S. Ki,* Gyeongsang National University, Republic of Korea*; J. Yun,* Jeonnam Bioindustry Foundation, Republic of Korea*; S. Jung,* Sunchon National University, Republic of Korea

Hydrogen is firmly recognized as a future clean energy that will replace fossil fuels and solve environmental pollution. However, most of the H_2 production still depends on steam reforming using fossil fuels or natural gas. In order to realize a future H_2 energy society, it is necessary to develop a technology that can produce a large amount of H_2 using renewable energy. CO_2-free H_2 production is essential for this technology. This study was conducted the cracking of waste hydrocarbons. Plasma was directly discharged to liquid reactant. Synthesized perovskites and metal oxide were introduced as catalysts. The correlation between the reaction results according to the characteristics of the catalyst was investigated.

Catalytic properties of perovskites were proposed in the decomposition of waste hydrocarbons using liquid-phase plasma (LPP) for H_2 production. Perovskite-type catalysts and metal oxide catalysts were applied to the cracking reaction. Hydrogen was generated by decomposing the liquid hydrocarbons by the LPP. The only gaseous product was H_2 and no CO_2 was formed. As a solid product, nano-sized carbon containing no impurities was produced.

Decomposition of waste organic solvents was performed in a liquid-phase plasma reaction system connected to a mass flow meter (MFM) and a gas chromatograph (GC). Benzene, toluene, and n-hexane were used as reactants. The H_2 production rate was measured using MFM. GC was used to analyze the composition of the gaseous product. Plasma was emitted between the two electrodes filled with liquid reactant and catalyst.

The only gaseous product was H_2 and no CO_2 was formed. As a solid product, nano-sized carbon containing no impurities was produced. The H_2 production rate and carbon yield obtained by reacting for 1 h under liquid plasma irradiation was measured. About 35 L/h of H_2 was obtained even under no catalyst condition. The yield of carbon black was also about 10%. It was further increased in the perovskite catalysts. TEM image of carbon produced as the reaction time elapsed was measured. The carbon products were similar in crystal shape and size regardless of the reaction time. The crystal size was small and uniform (10 nm or less). The H_2 production rate was greatly increased on perovskite catalysts. The yield of carbon black was also improved.

PS-TuP-3 Tailoring of Mg Thin-Film Corrosion Properties with Dielectric Barrier Discharge Plasma Treatment*, Lisa Hanke*, *T. Hartig, F. Weisheit, T. Tjardts,* Kiel University, Germany*; M. Valtiner,* Vienna University of Technology, Austria*; F. Faupel, E. Quandt,* Kiel University, Germany

Magnesium based implants are studied as biodegradable alloys with the possibility to release therapeutically relevant ions such as lithium locally in the body. For degradation and, thus, corrosion, the surface structure and composition play a significant role and can be used to adjust the corrosion rate and ion release Techniques such as plasma electrolytic oxidation using a liquid electrolyte are well studied to change surface properties, also for MgLi alloys. However, symmetric volume dielectric barrier discharge (DBD) plasma treatments without additional precursors are not widely investigated. DBDs are scaled up in industrial applications and allow a fast and cheap surface treatment at atmospheric pressure. It is known to modify surface properties such as the wettability and effect the surface chemistry. In this study, the effect of DBD plasma on Mg based thin films as an easy and fast surface treatment for controlling the corrosion rate and ion release is investigated. Mg and MgLi based thin films with a Li content of 5.4 at% and 26.9 at% are produced by magnetron sputtering and are treated with DBD plasma for different treatment times between 5 and 30 seconds with fixed plasma parameters. The influence on the surface topography is measured by SEM and the composition of the film by EDX and XPS. After the plasma treatment, a thin layer is formed on the surface which exhibits small cracks for the longest treatment time. This layer can be identified by XPS measurements as carbonate and oxide components in higher amounts than for the untreated samples. If those surface films are stable during corrosion, they slow down the degradation and ion release. The corrosion rate is determined by potentiodynamic polarisation measurements in Hanks' balanced salt solution at 37 °C and pH 7.4. By in situ measurements with an electrochemical flow cell connected to inductively coupled plasma – mass spectrometry (ICP-MS) the ion release is determined. It can be seen that the corrosion rate is decreasing with longer treatment time and is only half of the corrosion rate of an untreated sample after a treatment for 15 seconds. For all samples, a high increase of lithium release is determined at the beginning while magnesium release is stable which identifies a surface layer with high Li content. However, identification of ion release over long open circuit potential (OCP) measurements and at potentials above the OCP allow further analysis of the influence of the treatment. The results show a slower ion release and stronger passivation for plasma-treated films which support the idea of the formation of a protective layer.

PS-TuP-4 Improvement of Reliability in a-IGTO Thin-Film Transistors by H_2S Plasma Treatment*, Jin-Hwan Hong*, *D. Kim, B. Choi,* Sungkyunkwan University (SKKU), Republic of Korea

In this work, amorphous induim-gallium-tin-oxide thin-film transistors (a-IGTO TFTs) with H_2S plasma treatment was demonstrated for the first time.

Through the H_2S plasma treatment, both the electrical performance and reliability of the a-IGTO TFTs were improved. The carrier mobility and bias stress under temperature significantly increased with the H_2S plasma treatment, which is due to the incorporated sulfur not only providing an extra electron to the a-IGTO, but also passivating the interface trap density induced by exceeded oxygen vacancies. In addition, by conducting the a-IGTO TFTs with H_2S plasma treatment, the hyteresis effect of the TFTs has been improved and tolerance of the TFTs against moisture from the ambient atmoshphere has been improved. We believe that the proposed H_2S plasma treatment is suitable for the efficient fabrication of oxide semiconductor-based TFTs, as well as for accelerating the electrical performance and reliability of their electrical characteristics in a wide range of modern applications such as oxide semiconductor-based flexible and display electronics.

PS-TuP-5 Effects of Plasma Induced by Extreme Ultraviolet (EUV) Radiation on the Material Surfaces*, **Juyoung Jung**, J. Hong,* Sungkyunkwan University (SKKU), Republic of Korea*; H. Park, Y. Jung,* Samsung Electronics Co., Inc., Republic of Korea*; B. Choi,* Sungkyunkwan University (SKKU), Republic of Korea

Currently, the extreme ultraviolet (EUV) plasma, which is one of the laser produced plasma, is an essential fabrication for producing miniaturized integrated circuits in semiconductor manufacturing processes. The tin plasma produced by CO_2 laser emits high energy photons of 92 eV through electron transition to a lower energy state. Both plasma and photon of high energy excite molecules or atoms to produce highly reactive ions or ligands, and create particles to contaminate most parts in beam path. The environment of the equipment that generates EUV light maintains a high vaccum state, including approximately 5 bar of gas. These gases turn plasma with extremely high energy, and permeates the surface of liquid tin and solid materials. As a result, highly reactive plasma permeates and accumulates under the surface of the material. When the plasma release onto the material surfaces, it becomes a contamination sources. In this paper, we have researched the contamination mechanism and solution of the material surface in EUV system. To reduce the contamination generated by plasma, we have experimented with various types of method such as materials, voltage, shape of patterns, and arcing. We believe that various experiments and results will provide a method to control contaminants by plasma in the EUV system.

PS-TuP-6 Effects of Ambient Air Conditions on Characteristics of Decomposing Aqueous Phosphorus Compounds by a Pin-to-Liquid Dielectric Barrier Discharge*, **Gyu Tae Bae**, J. Kim, E. Jung, H. Jang,* Kyungpook National University, Republic of Korea*; D. Kim, H. Lee,* Electronics and Telecommunications Research Institute, Republic of Korea*; H. Tae,* Kyungpook National University, Republic of Korea

Recently, non-thermal plasma (NTP) has proved to be an important tool for efficient water treatment [1]. In particular, NTP generated in the gas–liquid phase can produce in situ highly reactive species such as N_2, NO•, O_2, H_2O^+, OH^-, OH•, H_2O_2 which contribute to the decomposition of organic materials [2]. Among the various NTP sources, the pin-to-plate discharge is one of the simplest methods to effectively generate NTP containing reactive species radicals at atmospheric pressure. The pin-to-plate electrode configuration allows for easy air discharge without additional gas discharge due to the pointed tip of the pin-shaped electrode, which induces local electric field enhancement. As this NTP device has a simple structure and is easy to control, which is advantageous for device miniaturization.

More recently, a pin-to-liquid dielectric barrier discharge (DBD) structure using a water-containing vessel body as a dielectric barrier for total phosphorus monitoring in water has been reported [3]. In this study, characteristics of water treatment using a pin-to-liquid DBD structure are investigated in three different ambient air conditions: open atmosphere, closed atmosphere, and closed atmosphere with air flow. The results showed that the changes in pH and electrical conductivity with plasma treatment time are highly dependent on the ambient air conditions, when the electrical input is kept the same for all systems. Since the proposed pin-to-liquid DBD structure does not use any additional discharge gas except for the atmosphere, the generated reactive nitrogen species originates from the atmosphere and its amount also varies with atmospheric air conditions. As a result, we observed that the water treatment efficiencies were different under three different atmospheric air conditions by comparing the decomposition properties of phosphorus compounds. In addition, we demonstrate that the decomposition performance of phosphorus compounds comparable to that of an open atmosphere can be obtained by circulating a few air flows in a closed atmosphere.

References

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PS-TuP-7 Influences of Asymmetric Bipolar Voltage Pulse on Film Properties of Polypyrrole Prepared by Solution Plasma Process*, **Hyo Jun Jang**, E. Jung, J. Kim, G. Bae, H. Tae,* Kyungpook National University, Republic of Korea

A solution plasma process uses intermediate products generated by the interaction between an ionized gas (plasma) and solution substances for material processing [1]. The process that generates plasma in liquid maximizes the plasma-liquid interface and concentrates plasma energy into the reaction because the plasma avoids quenching by air. Most plasma reactors that generate in-liquid plasma are designed with a pin-to-pin type electrode structure facing each other at a narrow distance in a solution to facilitate discharge [2]. This electrode configuration generates an instantaneous strong discharge, causing activation of the liquid molecules to create intermediate products. As these intermediates move away from the plasma source, they passivate in the form of nanoparticles based on themselves in solution. Recently, the solution plasma reactor having a pin-to-surface electrode structure with the argon gas addition has been proposed to control excessive plasma energy and generate stable plasma in solution [3]. The presence of the surface-type electrode enables film deposition as well as nanoparticle synthesis in solution.

In this study, we observed that a polypyrrole (PPy) film can be deposited on the surface electrode in liquid pyrrole by a solution plasma process in which a negatively biased bipolar voltage pulse is applied to the pin electrode. The plasma generated during the negative period of the applied waveform produces pyrrole anions that do not react with the pyrrole solution. Instead of forming PPy nanoparticles in a pyrrole solution, they drift and deposit onto the surface electrode as relative anode by the negatively biased voltage applied to the pin electrode. In PPy film synthesis using the solution plasma process, an asymmetric voltage waveform with a larger negative magnitude is essential, and the generation of pyrrole anions in the solution plasma depends on the negative amplitude of the driving waveform. In the solution plasma process with the pin-to-surface electrode, the effects of the negative amplitude of asymmetric bipolar waveform on PPy film properties are investigated in detail.

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PS-TuP-8 Liquid Crystal Alignment Effect in Inorganic Alignment Layer Applied with Atmospheric Pressure Plasma*, **Jin-Ah Kim**, S. Choi,* Department of Smart Manufacturing Engineering, Changwon National University, Republic of Korea*; H. Park,* Department of Electrical, Electronic, Control Engineering, Changwon National University, Republic of Korea

The liquid crystal alignment process has a great impact on the performance of liquid crystal displays (LCDs). As a liquid crystal alignment method, various liquid crystal alignment methods such as an oblique deposition method, an ion-beam deposition method, and a photo-alignment method have been studied, but they have disadvantages in that the equipment required for the process is expensive and an additional cleaning process is required. Recently, studies for applying atmospheric pressure plasma to liquid crystal alignment have been actively conducted.

In this study, by applying atmospheric pressure plasma as an alignment method, the liquid crystal alignment effect on the alignment layer doped with various kinds of inorganic nanoparticles was confirmed. It was confirmed that the alignment was made uniformly without partial defects through observation under a polarized light microscope. The pretilt angle was measured using a crystal rotation method to confirm the LC arrangement. Surface contact angle measurement allows observation of changes in surface modification after atmospheric pressure plasma treatment. Voltage-transmittance characteristics and response time were measured by electro-optical characteristics. Through this study, it was possible to confirm the liquid crystal alignment effect of atmospheric pressure plasma in the inorganic alignment layer, and the possibility of industrial application was confirmed.

PS-TuP-9 Effect of Atmospheric Plasma - Rubbing Treatment on the Liquid Crystal Alignment on Inorganic Layer

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Liquid crystal alignment is one of the important technologies in fabrication liquid crystal display (LCD), and lots of research is being done. This technology has an important role in controlling the light transmitted from the backlight and has been established as an essential technology in the fabrication process. Inorganic alignment layers that can replace the conventional polyimide (PI) alignment layer have been studied in advance. We confirmed the effect on liquid crystal alignment by performing the plasma-rubbing method as a process variable on the inorganic alignment layer, respectively. We measured LV-SEM to confirm the deposition of the alignment layer on the surface of the fabricated cell, the uniform alignment was confirmed through a polarized light microscope, and the contact angle was measured to confirm the modification change on the surface. In addition, the pre-tilt angle was checked, and the UV/Vis transmittance measurement for the transmittance analysis in the visible ray band and the electro-optical characteristics such as voltage-transmittance and response time were measured.

PS-TuP-10 Deposition and Characterization of Carbon Nanowalls Synthesized by Microwave Discharge System Using Different Carbon Sources

K. KWAK, ***Abdessadk ANAGRI****, F. BOHLOOLI, S. MORI,* Dept. of Chemical Science and Engineering, Tokyo Institute of Technology, Japan

In this study, we synthesized carbon nanowalls by microwave plasma-enhanced chemical vapor deposition system using different feed gas mixtures CO/H_2 and CH_4/H_2 system. Carbon nanowalls (CNWs) are interconnected stacks of graphene sheets that oriented vertically on a substrate; each sheet is composed of a few layers of graphene with length and height ranging from a few nanometers to microns.is micrometre-wide freestanding flakes consisting of stacked graphene layers. The experimental apparatus used in this study is the same as that in the previous study [1]. The microwave plasma-enhanced CVD system is a modified ASTeX DPA25 plasma applicator in which the quartz discharge tube of a 15 mm inner diameter is utilized. The maximum power of microwave source is 250 W. Silicon single crystal wafers were used as substrates with a size of 10×10 mm2 square. No catalyst materials were used in this study. The parameters of the CNWs deposition process were as follows: CO flow rate, 0-50 sccm; H_2 flow rate, 0-50 sccm; CH_4 flow rate, 0-50 sccm; total pressure, 20-250 Pa; microwave power, 60-120 W. The plasma emission was monitored by a spectrometer. Carbon deposits grown on the substrate were observed by scanning electron microscopy and transmission electron microscopy and analyzed by Raman spectroscopy. It was found that the CNW synthesized using CO has a larger flake size than the CNW from CH_4 as a carbon source. Generally speaking, the flake size was larger when hydrogen was present at higher concentrations. We have analyzed the crystallinity of CNWs by the Raman spectroscopy. The crystallinity of the CNW is evaluated by the intensity ratio of D peak which relates to the disorder and G peak which means the presence of crystalline graphene layers, ID/IG, and half width of G peak, WG. Here, a low ID/IG value and a small half width WG of the G peak indicate good crystallinity. As you can see these results, we can find Id/Ig of CO CNWs is lower and half width of CO CNWs is also lower than CH4 CNWs. Therefore, it is concluded that the CNWs synthesized using CO have a more crystalline graphene layers. We will discuss the reason why CO CNWs have more crystalline graphene layers than CH4 CNWs. One of the possible reasons for the difference in the crystallinity comes from the amorphous carbon etching ability of hydrogen and oxygen. When CH4 is used as carbon source, only H is present in the reactor, while when CO is used as carbon source, O and H are present. And since oxygen has a higher ability to etch amorphous carbon,CNWs synthesized from CO have more crystalline graphene layers than those from CH4.

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