

Thursday Afternoon Poster Sessions

Plasma Science and Technology

Room: Southwest Exhibit Hall - Session PS-ThP

Plasma Science and Technology Poster Session

PS-ThP1 Transition in Intensities of the Forbidden Atomic Oxygen Spectral Lines and its Application to Plasma Monitoring. V. Milosavljevic, Dublin City University, Ireland & University of Belgrade, Serbia, A. Jasenko, Faculty of Pharmacy, Serbia, Z. Simic, L.C. Popovic, Astronomical Observatory, Serbia

To decouple the optical contributions of surfaces in a process chamber to the plasma chemistry from those of other constituents present in the plasma is one of the most demanding tasks today. In this work oxygen spectral emission is used for purposes to increase understanding of plasmas such as those used in industry and particularly those used in semiconductor device manufacture, when plasma-surface interactions are of critical importance.

We analyze the intensity of forbidden oxygen lines at 630.0, 636.3, 297.23 and 557.73 nm as well as the (NLTE afflicted) oxygen triplet lines around 777.4 nm. The emission of forbidden spectral lines is used to establish a threshold for actinometry. Actinometry suffers from signal masking by molecular species due to molecular dissociation and trace gas emission. To establish the threshold for actinometry we monitor the emission of forbidden spectral lines and search for "phase transition" in the intensities of forbidden spectral lines (in most cases the upper energy levels of atomic forbidden lines are below the threshold for dissociation of any constituent molecule so that any sudden increase in the emission intensity of forbidden lines indicates molecular dissociation has occurred). Concurrently the forbidden spectral line is used for determination of the main plasma parameters too.

Radiative emission of the forbidden spectral lines follows a three level atomic model that characterizes the radiative transfer processes, and can help to understand the contribution of molecular dissociation processes to the emission spectrum of atomic oxygen. This represents a major contribution to the current state of the art and eliminates the requirement for trace gas based actinometry which will overcome not only the molecular masking problem but the intrinsic problem of having a trace gas in the plasma discharge. Thus, this work develops the method based on OES as a non invasive technique for quantifying complex chemistry which has direct application in plasma processing in semiconductor and other industries. This approach enables greater understanding of complex processes allowing, optimization, fault detection, increased productivity and yields. The challenge in this case lies in the complex plasma chemistry that is commonly used in surface treatment and the constraint of applying intrusive sensors to industrial plasma reactors. These constraints make OES ideal for industrial use, however interpreting the spectra and extracting useful information is the challenge. This work is done with ICP 13.56 MHz RF plasma discharge at pure oxygen, as well as oxygen-argon-hydrogen mixture.

PS-ThP2 Optical Emission and Mass Spectrometric Characterization of a Dual Plasma PE-CVD System. Z. Chen, V.M. Donnelly, D.J. Economou, University of Houston

Initial diagnostic studies will be presented of a novel PE-CVD reactor suitable for self-limiting growth of thin films through a repetitive, step A / step B, process. In a single vacuum system, two independent plasma sources are operated to separate step A from step B. An Ar gas curtain minimizes mixing of the gases of the two plasma sources. As an example, this reactor could be used to deposit a very thin hydrogenated amorphous silicon (a-Si:H) film in step A, followed by exposure of this film to a hydrogen plasma in step B, to induce formation of silicon nano-crystallites. In the present reactor configuration, one plasma source is a capacitively-coupled plasma (CCP) reactor and the other is an inductively-coupled plasma (ICP) reactor. The substrate is moved back and forth between the two sources. Optical emission spectroscopy (OES) and mass spectrometry (MS) are used to detect radicals (OES) and stable feed gas and products (MS) in the two plasma sources. Results will be presented for a SiH₄/He CCP and H₂, N₂ or O₂ ICPs operating simultaneously. The degree of separation of the two plasma sources will be presented as a function of the Ar flow rate to the gas curtain, as well as the feed gas flow rates and pressures of the plasma sources.

PS-ThP3 Diagnosis of Gold Nanoparticle Synthesis in Solution Plasma by Coherent Anti-Stokes Raman Spectroscopy. D. Fujimoto, J. Hieda, M.A. Bratescu, O. Takai, N. Saito, Nagoya University, Japan

The performance of the electrical discharges in the aqueous solution presents modern and ecologically very attractive way of the synthesis of nanoparticles. Such kind of techniques are known for the production of very active species like hydrogen radicals, hydroxyl radicals, ozone, aqueous electrons, UV light, etc., which are characterized by its very high reactivity. Although both oxidation and reduction agents were generated in the plasma, gold, platinum, and copper ions were reduced by the plasma. In order to control the reactions in solution plasma, the understandings of activated species and their behaviour are needed.

In this paper we present process diagnosis of gold nanoparticles synthesis in solution plasma based on coherent anti-stokes Raman spectroscopy (CARS). This discharge is generated between two wire type electrodes faced one to each other and driven by bipolar dc pulse power supply. Utilization of this power supply gave us a possibility of an intensive and stable working condition even at lower liquid conductivities. Operation conditions of this power supply lie in the frequency range 0-50 kHz, with minimum pulse length, 2 ms, and maximum voltage, 1.5 kV. In order to obtain desired conductivity of liquid, a small amount of KCl was added into the water. Initial [AuCl₄⁻] concentration and pH were varied. The reactor was placed on the stage of the optical microscope with CARS system. The morphology of the nanoparticles obtained was observed by transmission electron microscopy (TEM). The solution after discharge was also analyzed by UV-Vis spectroscopy and ICP-MS.

PS-ThP4 Characterization of a Faraday-shielded Inductively Coupled Plasma using Langmuir Probe and Optical Emission Spectroscopy. W. Zhu, H. Shin, L. Xu, V.M. Donnelly, D.J. Economou, University of Houston

A novel plasma reactor was designed and built to control the electron energy distribution function (EEDF) in the plasma, as well as the ion energy distribution (IED) and ion angular distribution (IAD) on the substrate electrode. The main inductively coupled plasma (ICP) source has a Faraday shield to minimize the RF component of the plasma potential. The substrate electrode and another electrode in contact with the plasma (boundary electrode) can be biased independently with DC or RF voltages to influence the IED and IAD. A second tandem ICP plasma source may be used to inject a secondary plasma or metastable atoms to the main source, to influence the EEDF. A continuous wave argon plasma in the main ICP was characterized with a Langmuir probe (LP), with and without the Faraday shield installed. With the Faraday shield, the DC value of the plasma potential decreased from 25 to 17 V, and the corresponding peak-to-peak amplitude of the RF oscillation dropped from ~15-20 V to ~0.8-1.5 V, compared to the case without the Faraday shield. A low plasma potential is critical for certain processes such as atomic layer etching with monolayer precision. The electron "temperature" as well as the ion and electron densities were measured for a range of powers and pressures. The plasma density was $1.5 \times 10^{12} \text{cm}^{-3}$ at 40 mtorr and 300 W. The EEPF was also measured with the LP; comparisons with EEPFs extracted using trace rare gas-optical emission spectroscopy (TRG-OES) will be presented. In addition to argon, oxygen and krypton plasmas were studied and their similarities and differences with the argon plasma will be shown. Control of the plasma potential and hence energy of ions impacting surfaces was achieved by applying a positive DC voltage to a boundary electrode immersed in the plasma. Finally, preliminary results of plasma injection from the secondary to the main plasma source and its effect on the EEDF will be presented.

Work supported by the Department of Energy Plasma Science Center and NSF

PS-ThP5 Diagnostic of Laser Ablation Air Plasma using Wide Field Spectroscopy. N. Abundiz, UNAM-CICESE, Mexico, C. Velez, UABC, Mexico, E. Luna, S. Zazueta, Universidad Nacional Autónoma de México, R. Machorro, Universidad Nacional Autónoma de México

Plasmas generated by pulsed laser have a brief existence and their properties are far from uniform. Optical spectroscopy provides information about the spatial and temporal evolution of transient species produced by the laser-matter interaction, such as excited atoms, ions or molecules. This knowledge is essential to understand the ablation phenomenon, and develop better models.

In this work, we use a Nd-YAG laser with 3J energy, 1064nm wavelength, and 7 ns duration pulsed beam, focused with a 20cm focal length biconvex lens into ambient air. Fluence of the order of $3 \times 10^6 \text{ J/m}^2$ creates an electric field of $3 \times 10^9 \text{ V/m}$, enough to ionize the air atoms, creating a plasma.

A camera lens forms the plume image into the image plane, where an optical fiber array with 12*12 fibers is placed. The array is re-arranged to form a one-dimensional column with 144 fibers, which becomes the entrance slit of the spectrograph. A gated image intensified CCD captures the output plane of the spectrograph. An electronic device produces a precise time delay between laser pulse and image capture. From this data it is possible to get density and temperature maps of the species, and its discrete time evolution. Moving the camera lens and fiber array along the optical axis, we make a confocal scanning of the plasma.

In the high density regime, the plasma is dominated by collisions, and intensity ratios of lines from the same ion will depend exclusively on the temperature in the manner prescribed by the Boltzmann distribution. We present reconstruction of spectral images of the plasma, as a function of time and axial displacement.

Partial support from the CONACyT project 60351 and DGAPA-UNAM project IN100910 is acknowledged, student NA thanks Conacyt for her scholarship.

PS-ThP6 *In-situ* Monitoring of Organic Pollutants Degradation in Pulsed Plasma by Coherent Anti-Stokes Raman Spectroscopy, M.A. Bratescu, N. Saito, O. Takai, Nagoya University, Japan

Water pollution and storage is becoming an important problem to the people worldwide. Conventional water treatment processes, such as chlorination and ozone oxidation suffer a lot of limitations. The application of pulsed electrical discharges in water solutions for degradation of organic pollutants offers the advantage of simultaneous using of different physical effects (UV light) and chemical effects by the active species like OH, H, O, HO₂, H₂O₂, O₃ able to decompose the harmful organic compounds. In this study we analyzed the degradation of the benzoquinone molecule by using *in-situ* Coherent anti-Stokes Raman Spectroscopy (CARS) in order to monitor the active species during the decomposition process.

In the present experiment a pulsed plasma in an aqueous benzoquinone solution was used. The plasma was generated in a reaction glass cell, between two rods electrodes. The plasma electrical characteristics were: the peak to peak voltage of 2 – 4 kV, the pulse frequency of 10 – 15 kHz and the pulse width of 2 μs. The reaction cell was set on the optical microscope stage of the CARS system. Benzoquinone was dissolved in a potassium sulfate solution (4 g/L) and the pH was adjusted with dilute sodium hydroxylate or dilute sulfuric acid.

The CARS benzoquinone signal was observed at 1230 cm⁻¹, 1050 cm⁻¹ and 1667 cm⁻¹ corresponding to COH bending CH, bending and CC stretching vibrations, respectively. Degradation of the benzoquinone molecule was monitored by the peak at 1667 cm⁻¹, characteristics to benzene ring vibration. The shift and the amplitude of the absorption peak at 427 nm were observed by *ex-situ* measurements by the UV-visible spectroscopy.

The degradation of benzoquinone molecule depends on solution pH and plasma electrical characteristics.

PS-ThP7 Study of Plasma-based Ion Implantation Sterilization using High Resolution Rutherford Back Scattering, T. Tanaka, T. Hironaka, Hiroshima Institute of Technology, Japan, S. Hayashi, Japan Medical Creative, Japan, I. Koyama, Saitama Medical University, Japan

Plasma base ion implantation (PBII) with negative voltage pulses to the test specimen has been applied to the sterilization process as a technique suitable for three-dimensional work pieces. Pulsed high negative voltage (5μs pulse width, 300 pulses/s, -800 V to -13 kV) was applied to the electrode in this process at a gas pressure of 2.4 Pa of N₂. We found that the PBII process reduced the numbers of active *Bacillus pumilus* cell using N₂ gas self-ignited plasma generated by only pulsed voltages. The number of bacteria survivors was reduced by 10⁻⁵ x with 5 min exposure. As the ion energy is the most important processing parameter, a simple method to estimate the nitrogen ion energy calculated using distribution for nitrogen in Si implanted by PBII was estimated. The ion implanted surface using PBII sterilization is discussed from measurements data using the High Resolution Rutherford Back Scattering (HR-RBS).

PS-ThP8 A Novel Current-Voltage Probe for Diagnostics in Deposition Plasma, M.B. Hopkins, D.M. O'Sullivan, Impedans Ltd., Ireland

Current-voltage probes monitor power parameters, such as the voltage, current and phase angle of an RF power used to generate the plasma (source) or to bias a substrate. A number of commercial systems are available and a key feature is that the sensors work in non-50Ω environment. This allows the sensor be placed either pre-match or post-match and still make accurate measurements.

The most important plasma parameters in a capacitively coupled plasma source or bias configurations are the flux and energy of ions arriving at the substrate. The ion flux is difficult to establish in deposition tools as the

plasma often deposits insulating layers, such as in the manufacture of solar panels.

We report on a novel IV sensor, which is placed post-match in series with a capacitively coupled RF biased plasma electrode. The sensor integrates the current into voltage bins. We show that the resulting characteristic represents the real current-voltage (IV) characteristic of the electrode. The measured IV trace is similar to a DC Langmuir probe IV trace and we determine the ion flux to the biased electrode. We compare ion flux measured by the IV probe with the ion flux determined by a retarding field analyzer placed on the electrode.

Other parameters such as electron temperature and plasma potential are also obtained and compared to direct measurements taken in the source.

PS-ThP9 Hardness and Roughness of SiCN Thin Films Deposited at 500 °C by RF-PECVD, T. Wydeven, T. Kawabe, SAMCO International, Inc.

The experimental difficulties encountered in attempting to synthesize super hard high purity polycrystalline or single crystal beta carbon nitride (β-C3N4) films has prompted research on the synthesis of hard silicon carbon nitride (SiCN) films(1). Current research interest in SiCN is motivated by several reported desirable properties of this material(2). Among those properties are short bond length, high bond strength and therefore high hardness, adjustable friction coefficient, high resistance to wear and corrosion and wide band gap.

The work reported on here is a continuation of our earlier research (3) on the deposition and characterization of near stoichiometric SiCN films deposited at ambient temperature from a gas mixture (SiH₄, CH₄, N₂) and using RF-PECVD. In this work, we report on the hardness and characterization of surface topography by roughness measurements and SEM photographs of SiCN films deposited at 500 °C on silicon wafer substrates using RF-PECVD. These measurements are important in applications involving friction, lubrication and wear(4).

References

1. J. C. Sung, *New Diamond and Carbon Technology* **12** (2002) 47.
2. Fei Zhou, Bin Yue, Xiaolei Wang and Lanjian Zhuge, *Journal of Alloys and Compounds* **492** (2010) 269-276.
3. T. Wydeven and T. Kawabe, *Deposition and characterization of silicon carbon nitride films prepared by RF-PECVD with capacitive coupling*, Proceedings of the 19th International Symposium on Plasma Chemistry, Bochum, Germany, July 26th-31st, 2009.
4. T.R. Thomas, *Rough Surfaces*, 2nd ed., Imperial College Press, London (1999).

PS-ThP10 The Role of Negative Oxygen Ions in the Pulsed-Plasma Deposition of Titania Films, J.W. Bradley, R. Dodd, S.D. You, University of Liverpool, UK

Reactive pulsed magnetron sputtering is the process of choice to deposit commercially important oxide-based thin films and coatings. The technique relies on the plasma ions (e.g. Ar⁺, O⁺) assisting the deposition process through energetic impact at the substrate leading to good, dense coating structures.

However, in these systems copious amounts of negative ions (O⁻, O₂⁻, O₃⁻, MO_x⁻) can be created at the cathode target. These ions are accelerated through the cathode sheath to bombard the substrate with upper energies equivalent to the target potential, (i.e. hundreds of eV). These ions easily overcome the negative substrate bias potentials, used to attract positive ions and can be wholly destructive to growth of engineering quality films.

In this study we use an eclipse laser photo-detachment technique combined with a Langmuir probe to measure the density of negative ions in the pulsed sputtering of titanium in oxygen-argon mixtures. This has been done at different positions in the plasma during different phases of the driving pulsed-voltage waveform. The results show that the total negative ion density can exceed that of the electrons and at positions close to the substrate on the discharge centre line, the fraction of very fast negative ions can be over 10% of the total observed. The power fluxes of these species at the substrate have been calculated and the effect on the growing TiO₂ film is discussed.

PS-ThP11 Investigation of the Plasma Parameters and Plasma Process-Induced Damage in Physical Vapor Deposition, X. Tang, T.-J. Gung, S. Gandikota, P. Gopalraja, R. Wang, G. Liu, Applied Materials Inc.

The introduce of the high K and metal gate enables significant gate leakage reduction (>100x) with excellent transistor performance. Physical vapor deposition process plays an important role in its manufacturing process because of its film composition tunability, excellent step coverage and thin film uniformity. However there are growing concerns about the potential

process damage induced by the physical vapor deposition process since in some cases these films are directly deposited on thin (~20Å) high k films. It is well known that PID can be classified into three categories: charging damage by plasma non-uniformity, bombardment damage by high energy ions, neutrals, and electrons, and radiation damage from plasma emission. In this paper, we mainly focus on high energy components in plasma itself and the process induced damage caused by the plasma non-uniformity. Both the discharge plasma properties (such as n_e , T_e , target voltage, ion energy etc) and their correlations to the potential plasma process induced damage were discussed. Two types of PVD chamber designs were evaluated in this study. One is a short throw rf PVD chamber which has both RF and DC power capability on the sputtering target. Another one is a long throw dc sputtering chamber with a special high ionization magnetron. Ti target material is used in this study. Discharge plasma parameters such as (plasma density n_e , electron temperature T_e , and plasma potentials V_{pl}) were monitored by a Langmuir probe inserted into the discharge cavity. The corresponding neutral and ion energy were further derived based on the measured target voltage and wafer self-induced dc bias. The plasma uniformity is characterized by an ion current probe biased at the ion saturation region. Two test vehicles: the 'Spiders' wafer with different ANT ratios and MOS cap were used to quantify the plasma process induced damage.

Langmuir probe studies show that the rf plasma density increases linearly with the rf power while

the electron temperature remains constant in RF PVD chamber. Very high metal ionization was achieved as a result of the high plasma density by high rf power and high pressure (>50mT) operation. Interestingly, no plasma process induced damage were observed by RF PVD Chamber under a broad range of process conditions even with different ion energy. On the other hand, with the dc high ionization (magnetron with a $UB > 3.5$) operation, significant plasma damage was observed under most conditions. The damage was later correlated to the plasma non-uniformity. These results clearly demonstrate that plasma non-uniformity needs to be optimized for any PVD hardware for the damage sensitive applications.

PS-ThP12 Realization of Silicon Antireflection Subwavelength Structure using Simple One Step Plasma Fabrication Process, B.S. Kim, J.H. Sung, M.W. Lee, C.H. Choi, H.D. Yim, S.G. Park, S.G. Lee, E.H. Lee, B.H. O, INHA University, Republic of Korea

Polished flat silicon surfaces have high reflectivity in visible rays. The minimization of reflection losses is very important for solar cells. Lowering surface reflectivity of silicon by texturization is one of the most important processes for improving the conversion photovoltaic efficiency of silicon solar cells.

Many texturing techniques for fabricating antireflective silicon surfaces have been proposed, including mechanical diamond saw cutting, optical interference lithography, wet etching using catalysis of metal, and reactive ion etching, to produce so-called "black silicon".

In this paper, we attempted to one step etching for formation of black silicon using combined Cl_2 , C_4F_8 , and O_2 gases. It uses inductively coupled plasma (ICP) and Cl_2 gas for etching, C_4F_8 and O_2 gas for masking.

The substrate temperature was $-10\text{ }^\circ\text{C} \sim 10\text{ }^\circ\text{C}$, the fluorocarbon film deposited in a C_4F_8 plasma was thicker and more strongly bonded than the lower substrate temperature. Then combined O_2 gas, fluorocarbon film was locally etching which is self-masking effect. The diameter of fluorocarbon mask was dozens nanometer size.

With Cl_2 etching, many processes were developed for producing vertical sidewalls, smooth surface morphology, fine critical dimension control, and high aspect ratio microstructures for MEMS. The main advantage of Cl_2 etching is that etching is anisotropic since it is an ion assisted process rather than a spontaneous etching process. The subwavelength silicon pillar structure was grown up because physical etching characteristic of Cl_2 plasma.

The etched silicon surface shows almost zero reflectance in the visible region. The silicon surface is covered by columnar microstructures. The diameter and height of subwavelength silicon columnar structures were depends on substrate temperature, etching, and gas contain ratio.

PS-ThP13 Synthesis of Zinc Oxide Nanoparticles Using an Atmospheric Pressure Plasma Jet, S.M. Chang, C.C. Hsu, National Taiwan University, Taiwan, Republic of China

Nanocrystalline zinc oxide particles have been synthesized using a gas-phase process by atmospheric pressure plasma jets (APPJ). The APPJ used is sustained by a repetitive pulse source with nitrogen or oxygen as the plasma gas. Zinc-containing salt solutions, namely $Zn(NO_3)_2$ and $ZnCl_2$, are nebulized into μm -sized droplets and fed into the downstream of the APPJ. Liquid droplets undergo vaporization and reaction and form solid particles in the downstream of the jet. The particles are collected using de-ionized water or buffer solutions. The particle size and its distribution are measured

using the dynamic light scattering method and scanning electron microscopy. It is found that the reactivity and the temperature of the jet downstream are able to efficiently convert the droplets into crystalline ZnO particles, as confirmed by the X-ray diffractometer. When O_2 is used as the plasma gas, the fabricated ZnO particles readily dissolve in the particle-collecting solution due to the decrease in the pH of this solution. The pH drops to as low as 1 within 2 min. It suggests the need of using the buffer solution as the particle collector. When using N_2 as the plasma gas, a relative small change in pH is found and results in decent collection yield. When using $Zn(NO_3)_2$ solution as the precursor under 275 V applied voltage and 30 ~ 60 slm N_2 gas flow, the fabricated ZnO particles show a double-peak distribution: small and large particles with the averaged sizes of 120 nm and 1000 nm, respectively. Preliminary studies found that the particle size distribution can be altered by changing the precursor solution concentration, the carrier gas flow rate, and the plasma conditions. Finally, the potential using this apparatus to fabricate more complex metal oxides will be discussed.

PS-ThP14 Studies of Interactions between the Plasma in Salt Solutions and Organic Compounds, S.H. Wang, H.W. Chang, C.C. Hsu, National Taiwan University, Taiwan, Republic of China

Plasmas in salt solution have shown to be reactive due to the produce of reactive species such as OH, H, O, and H_2O_2 . In this study, interactions between the plasma in salt solutions and organic compounds are studied. The plasma is ignited in sodium-, zinc-, or calcium-containing salt solutions using DC or AC power sources. The electrode at which the plasma is ignited is a platinum wire 0.5 mm in diameter covered by a glass tube while the grounding electrode is a bare platinum wire of the same diameter. Cellulose, glucose and lactose are used as the organic compounds studied. Diagnostics include a voltage probe and a current probe to monitor the electrical characteristics; the conductivity and pH of the solution before and after the plasma treatment are monitored; an optical emission spectrometer is used to monitor the time-averaged emission spectra. It is observed that with the existence of the cellulose particles in the solution, the plasma appears to be much less stable. In addition, a much stronger light emission and larger current fluctuations are seen. This is possibly due to the fact that stable bubble is not able to form due to the existence of the cellulose particles. When glucose or lactose are added in NaCl solution, a much brighter plasma is seen and the optical emission shows a hump-like continuous emission band between 400–800 nm while this emission band does not exist without the addition of glucose and lactose. The total organic carbon (TOC) and high performance liquid chromatography (HPLC) measurements strongly suggest the possibilities that the cellulose, glucose, and lactose are decomposed due to the interaction with the plasma ignited in salt solution, especially when the plasma electrode is negatively biased. The identification of the decomposed products is currently underway. In this presentation, how the existence of the organic compounds influences the plasma behavior and how the organic compounds are decomposed in the plasma will be discussed.

PS-ThP15 The Optical Diagnostics of Microplasmas in Different Types of Electrolyte Solutions, A.H. Hsieh, C.C. Hsu, National Taiwan University, Taiwan, Republic of China

The optical diagnostics of microplasmas in various electrolyte solutions are performed. This microplasma is sustained by using a DC power source with the voltage up to 600 V. The powered electrode, the electrode where the plasma is ignited, consists of a thin platinum wire 0.5 mm in diameter covered by a glass tube. The grounding electrode is a bare platinum wire of the same diameter. Both electrodes are immersed in the solution. The electrolyte solutions studied include NaCl, $NaNO_3$, Na_2SO_4 , $ZnCl_2$, $Zn(NO_3)_2$ and $ZnSO_4$ with the concentration of 0.01 M ~ 2 M. Time-averaged optical emission and time-resolved intensities of the light emanating from the plasma are studied. With an applied voltage greater than 500V and the concentration below 0.02 M, there exists a bubble that stays steadily at the electrode tip for many seconds, and microplasma is ignited inside the bubble. Under this condition, the emission of H, OH, O and atomic metal emissions are observed regardless of the electrolyte type. In the high concentration conditions and low applied voltages, atomic metal emissions dominate and nearly no H, OH, and O emissions are seen. It is observed that for all electrolyte solutions studied except NaCl, there exist a hump-like continuous emission band in the optical emission spectra between 400–900 nm. The source of this continuous band is not identified yet but can potentially be a result of the thermal emission or free-bound transition. In this presentation, the implication of the optical emission to the plasma reactivity will be discussed.

PS-ThP16 Polyimide Surface Treatment by Using Atmospheric Pressure Plasma to Improve Metal Adhesion, J.B. Park, J.S. Oh, E.L. Gil, G.Y. Yeom, Sungkyunkwan University, Republic of Korea

Polyimide [(N, N'-oxydiphenylene) pyromellitimide], (PI) is one of the representative high-performance polymer films that has been widely used for the substrate in the microelectronic and flexible electronics industries because PI has desirable properties of high temperature resistance, good mechanical strength, and good dimensional stability. However, in spite of the extensive usage as well as the detailed characterization of the PIs, the poor adhesion of metals to PI, which is a consequence of its low specific surface energy, has to be overcome to render the fabricated devices reliable because the general polyimide-metal composites have limited adhesion strength. Therefore, many researchers have studied on the surface modification of PIs for adhesion improvement to metals.

In this study, the surface of PDMA-ODA PI films before and after atmospheric pressure plasma surface treatment by using remote type modified DBD module was investigated to improve the adhesion between the PI substrate and metal thin film using various gas compositions such as N₂/He/SF₆, N₂/He/O₂, N₂/He/SF₆/O₂, N₂/He/SF₆/O₂. Among the plasma treatments of the PI substrate surface using various gas mixtures, the plasma treatment with N₂/He/SF₆/O₂ showed the lowest contact angle value due to the high C=O bondings formed on the PI surface while that with N₂/He/SF₆ showed the highest contact angle value due to the high C-F_x chemical bondings on the PI surface. Especially, when O₂ gas was varied from 0 to 2.0 slm in N₂(40 slm)/He(1 slm)/SF₆(1.2 slm)/O₂ (x slm) gas composition, the lowest contact angle value of about 9.3° could be obtained at 0.9 slm of O₂ gas due to the highest oxygen radicals in the plasma, which forms the highest C=O bondings on the PI surface. When the interfacial adhesion strength between the Ag film and the PI substrate was measured after the treatment with N₂(40 slm)/ He(1 slm)/SF₆(1.2 slm)/O₂(0.9 slm) followed by the deposition of Ag, the peel strength of 111 gf/mm which is close to the adhesion strength between metal and the PI treated by a low pressure plasma could be observed.

PS-ThP17 Atmospheric Pressure Plasma Ashing of Photoresist using Remote-type Pin-To-Plate Dielectric Barrier Discharge, J.S. Oh, J.B. Park, E.L. Gil, G.Y. Yeom, Sungkyunkwan University, Republic of Korea

In these days, many researchers are developing glow discharges generated at atmospheric pressure for various thin films and surface processing such as dielectric barrier discharge (DBD), microwave discharge, pulsed corona plasma, etc. Various atmospheric pressure plasma sources have been reported with the claim of low running cost, low gas temperature, and wide applicability to surface treatment, cleaning, etching, and thin film deposition. Among the various atmospheric pressure plasmas, DBDs are studied mostly due to the easy generation of stable plasma.

In this study, ashing of photoresist (PR), AZ 1512, has been investigated using a pin-to-plate remote type DBD. The pin-to-plate type DBD showed higher power consumption and higher discharge current compared to the conventional DBDs at a given applied voltage. But glow discharge, which is generated by DBD, is easily transferred to filamentary/arc discharge, and the substrate is more likely to be damaged under arc discharge condition. Also, thermal damage can occur due to direct contact of the plasma to the substrate. But, remote plasma does not contact the substrate directly, therefore, the substrate can avoid damaging. In this study, using the remote type pin-to-plate DBD, the effect of various gas combinations such as N₂/O₂, N₂/O₂+SF₆ on the changes of PR etch rate and the electrical characteristics was investigated.

The addition of SF₆ gas to N₂/O₂ showed higher consumed power, higher discharge current at a given voltage, and lower turn-on voltage. For example, the plasma turn-on voltage for N₂ (50 slm)/O₂ (200 sccm) was 3.16 kV while that for N₂ (50 slm)/O₂ (200 sccm)/SF₆ (2.5 slm) was 2.7 kV, therefore, a lower turn-on voltage was obtained by adding 2.5 slm of SF₆. The consumed power for N₂ (50 slm)/O₂ (200 sccm)/SF₆ (2.5 slm) was 2330 W while that for N₂ (50 slm)/O₂ (200 sccm) was 1119 W. Therefore, the addition of 2.5 slm of SF₆ increased the power consumption in the plasma by ionizing and dissociation of the gas mixture further possibly through the penning ionization and dissociation. At N₂ (70 slm)/ O₂ (200 sccm) + SF₆ (3 slm), the maximum PR etch rate of about 1850 nm/min could be achieved.

PS-ThP18 SiO_x Thin Films Deposition by using a Modified Pin-To-Plate Dielectric Barrier Discharge Source in Atmospheric Pressure, E.L. Gil, J.B. Park, J.S. Oh, G.Y. Yeom, Sungkyunkwan University, Republic of Korea

SiO₂ films are used in various areas due to the excellent physical and chemical properties such as optical transparency, chemical inertness, scratch resistance, and sufficient hardness. In this study, as an application to a thin film passivation layer for flexible substrates, the deposition of SiO₂ thin film has been investigated. Especially, for the in-line and the roll-to-roll processing of flexible substrate, SiO₂-like thin film was deposited by an

atmospheric pressure plasma-enhanced chemical vapor deposition (AP-PECVD) technique at atmospheric pressure and at room temperature. A modified dielectric barrier discharge (DBD) called a "pin-to-plate-type DBD" having the combined characteristics of the remote-type DBD was used with a gas mixture of hexamethyldisilazane (HMDS)/O₂/He/Ar in order to generate high-density plasmas and to limit the damage to the substrate. The characteristics of SiO₂-like thin film were varied with gas mixture. As HMDS flow rate was increased, higher -(CH₃)_x bonds and lower -OH bonds were obtained due to the decreased recombination of carbon or hydrogen with oxygen, and consequently more particles and rough surface were observed. Although the increase of oxygen in the plasma was beneficial in removing all impurities relating to carbon, further increase of O₂ more than 14 slm obstructed forming the pure SiO₂-like films resulting in a rough surface. By using a gas mixture of HMDS (150 sccm)/O₂ (14 slm)/He (5 slm)/Ar (3 slm), SiO₂-like thin films with a low impurity could be obtained at a deposition rate of approximately 42.7 nm/min.

PS-ThP19 Studies of the Metal Electrode Erosion by Microplasmas in Saline Solution, C.Y. Sie, C.L. Chen, C.C. Hsu, National Taiwan University, Taiwan, Republic of China

The studies of the erosion of metal electrode by microplasmas in saline solutions are preformed. The plasma is ignited in saline solution of concentrations ranging from 0.01 to 2 M. This plasma is sustained by a DC power source with the voltage up to 600 V or a AC power source with the same voltage range and the frequency between 50 ~ 1000 Hz. The electrode on which the plasma is ignited is a metal electrode covered 0.5 mm in diameter by an alumina tube to precisely define the length exposes to the solution. The erosion of tungsten, titanium, and platinum electrodes is studied. During the plasma processing, the electrode erosion appears to be inevitable. It is found that when tungsten is used as the electrode, the most severe erosion occurs when the electrode is positive biased with the applied voltages at which no plasma is ignited, suggesting the electrolytic reaction plays an important role in the electrode erosion. With the plasma ignited at a higher applied voltage, increase in the applied voltage leads to a decrease in the erosion rate. When the AC power source is used, the erosion rate increases with the power frequency. In this presentation, the major erosion mechanism will be proposed and the strategy how the erosion rate can be minimized will be presented.

PS-ThP20 Formation of Size Regulated Platinum Nanoparticles Synthesized by Solution Plasma Process, T. Ishizaki, AIST, Japan, N. Saito, O. Takai, Nagoya University, Japan

Platinum nanoparticles have been applied to high activation of photo catalysis, catalysis for fuel cells, and cosmetics. Platinum nanoparticles have been synthesized by various techniques including chemical reduction, photo reduction and electrochemical technique. However, in these techniques, it takes few hours to synthesize the nanoparticles or chemically toxic substances leave in a product. Thus, it is required to develop an environmentally friendly technique to synthesize nanoparticles. We have developed 'Solution Plasma', which is defined as plasma in aqueous solution. Solution plasma has attracted much attention as a novel chemical reaction field. As solution plasma generates UV light, electrons, and radicals, it would reduce metal ions to nanoparticles without reduction agents. In this study, we aimed to synthesize platinum nanoparticles by solution plasma. In addition, we investigated influence of solution pH on the sizes of the platinum nanoparticles. Optical absorption of nanocolloidal platinum was measured by UV-vis spectrometer. The nanoparticles were observed by transmission electron microscopy (TEM).

H₂PtCl₆·6H₂O (1.44mM) and PVP (Polyvinylpyrrolidone, 12.1mM) were used as raw materials. The pH of solution was varied from 2.5 to 4.5. The electrical conductivity was adjusted to 1.5μS/cm by the addition of KCl. A pulsed power supply was utilized to generate plasma. Pulsed voltage of 1.6kV was applied between the tungsten electrodes in the solution. Pulse width and frequency were varied from 2.0 to 3.0μs, respectively.

Solution color changed from orange to dark brown at discharge times of more than 40 min. An absorption peak at 262 nm originated from PtCl₆²⁻ became weaker with the increases of the discharge time, while baselines in the spectra became higher in all the range. These results indicate the formation of platinum particles. TEM image shows that the mean diameter of the nanoparticles was 10nm. Debye rings by (111), (200), (220), (311) were also observed by diffraction patterns. The effects of pulse width, frequency and pH on the particle size distribution were also discussed.

PS-ThP21 Effects of Dirty Walls on the Plasma Potential of a Multi-Dipole Chamber, J.P. Sheehan, N. Hershkowitz, University of Wisconsin-Madison

In a multi-dipole chamber with dirty walls, the plasma potential is observed to be negative with respect to grounded wall in the tens of volts. The plasma

is generated by hot filaments releasing monoenergetic primary electrons ranging from 35 to 60eV. The primaries can exist in significant concentrations relative to the plasma electrons (up to 0.5% primaries as measured by a planar Langmuir probe) and contribute to charge neutrality, but not significantly to current balance. It is observed that the plasma potential becomes more negative with increasing relative concentrations of primary electrons. The potential profile next to the wall was measured using an emissive probe in the limit of zero emission[1]. The negative potential in the bulk plasma drops an additional few Te radially to the wall. The radial and axial potential profiles resemble those found in a chamber with clean walls and a positive plasma potential except the entire profile is shifted 10 – 20V lower. Possible mechanisms for these observations are suggested.

References

[1] J. R. Smith, N. Hershkowitz, and P. Coakley, Rev. Sci. Instrum. **50**, 210 1979.

PS-ThP22 New Solutions for Magnetron Sputtering Technology, M. Cichowlas, Huettinger Electronic, Poland

Traditionally, DC-pulsed units are advised to number of applications like: AZO, reactive sputtering with SN target, etc. This recommendation is based on the assumption that a DC-pulsed unit is enough to match process requirements.

Typical recommendations for usage of DC-pulsed units are as follows:

- high ARC rate,
- reactive process (reactive gas in the chamber),

The aim of this article is to introduce DC-non pulsed and High-Power (HIPIMS) units as more interesting alternative for expensive DC-pulsed units.

1. DC no-pulsed units

Advanced, powerful functions implemented into DC-non pulsed units, gives beneficial solution for processes affected by highly arcing materials like AZO. Ability to stable operation with extremely highly arcing frequency is one of most interesting features of DC power supplies developed by Huettinger Electronic. Mentioned units are able capably to work with 8000 ARCs/sec with 60kW output power.

Fig. 1. Behavior of AZO - extremely high arcing rates-70.000 arcs/s.

2. HIPIMS units

The other potentially interesting technique is HIPIMS coating. Looking for DC pulsed or DC non-pulsed processes, HIPIMS is going to serve fully dense, defect free films. Additionally, HIPIMS process leaves substrate temperature at lower level, compared to DC units. This gives a possibility for usage of completely new materials to be coated, like polymeric, foil or rubber. Moreover, power supplies for HIPIMS applications are equipped with CompensateLine (cable length compensation circuit), this allows to reduce arc energy to 0,3mJ.

Fig. 2. Behaviour of HIPIMS unit with arc during a HIPIMS pulse.

DC non-pulsed units can be used for advanced reactive processes, efficiently competing with DC pulsed units. The HIPIMS gives new possibilities for fully dense films on material required substrate temperatures.

Authors Index

Bold page numbers indicate the presenter

— A —

Abundiz, N.: PS-ThP5, 1

— B —

Bradley, J.W.: PS-ThP10, **2**

Bratescu, M.A.: PS-ThP3, 1; PS-ThP6, **2**

— C —

Chang, H.W.: PS-ThP14, 3

Chang, S.M.: PS-ThP13, **3**

Chen, C.L.: PS-ThP19, 4

Chen, Z.: PS-ThP2, **1**

Choi, C.H.: PS-ThP12, 3

Cichowlas, M.: PS-ThP22, **5**

— D —

Dodd, R.: PS-ThP10, 2

Donnelly, V.M.: PS-ThP2, 1; PS-ThP4, 1

— E —

Economou, D.J.: PS-ThP2, 1; PS-ThP4, 1

— F —

Fujimoto, D.: PS-ThP3, **1**

— G —

Gandikota, S.: PS-ThP11, 2

Gil, E.L.: PS-ThP16, 4; PS-ThP17, 4; PS-ThP18, **4**

Gopalraja, P.: PS-ThP11, 2

Gung, T.-J.: PS-ThP11, 2

— H —

Hayashi, S.: PS-ThP7, 2

Hershkowitz, N.: PS-ThP21, 4

Hieda, J.: PS-ThP3, 1

Hironaka, T.: PS-ThP7, 2

Hopkins, M.B.: PS-ThP8, **2**

Hsieh, A.H.: PS-ThP15, **3**

Hsu, C.C.: PS-ThP13, 3; PS-ThP14, 3; PS-ThP15, 3; PS-ThP19, 4

— I —

Ishizaki, T.: PS-ThP20, **4**

— J —

Jasenko, A.: PS-ThP1, 1

— K —

Kawabe, T.: PS-ThP9, 2

Kim, B.S.: PS-ThP12, **3**

Koyama, I.: PS-ThP7, 2

— L —

Lee, E.H.: PS-ThP12, 3

Lee, M.W.: PS-ThP12, 3

Lee, S.G.: PS-ThP12, 3

Liu, G.: PS-ThP11, 2

Luna, E.: PS-ThP5, 1

— M —

Machorro, R.: PS-ThP5, **1**

Milosavljevic, V.: PS-ThP1, **1**

— O —

O, B.H.: PS-ThP12, 3

Oh, J.S.: PS-ThP16, 4; PS-ThP17, **4**; PS-ThP18, 4

O'Sullivan, D.M.: PS-ThP8, 2

— P —

Park, J.B.: PS-ThP16, **4**; PS-ThP17, 4; PS-ThP18, 4

Park, S.G.: PS-ThP12, 3

Popovic, L.C.: PS-ThP1, 1

— S —

Saito, N.: PS-ThP20, 4; PS-ThP3, 1; PS-ThP6, 2

Sheehan, J.P.: PS-ThP21, **4**

Shin, H.: PS-ThP4, 1

Sie, C.Y.: PS-ThP19, **4**

Simic, Z.: PS-ThP1, 1

Sung, J.H.: PS-ThP12, 3

— T —

Takai, O.: PS-ThP20, 4; PS-ThP3, 1; PS-ThP6, 2

Tanaka, T.: PS-ThP7, **2**

Tang, X.: PS-ThP11, **2**

— V —

Velez, C.: PS-ThP5, 1

— W —

Wang, R.: PS-ThP11, 2

Wang, S.H.: PS-ThP14, **3**

Wydeven, T.: PS-ThP9, 2

— X —

Xu, L.: PS-ThP4, 1

— Y —

Yeom, G.Y.: PS-ThP16, 4; PS-ThP17, 4; PS-ThP18, 4

Yim, H.D.: PS-ThP12, 3

You, S.D.: PS-ThP10, 2

— Z —

Zazueta, S.: PS-ThP5, 1

Zhu, W.: PS-ThP4, **1**