Thursday Afternoon Poster Sessions

Plasma Science and Technology
Room: Hall D - Session PS-ThP

Plasma Science Poster Session

PS-ThP1 Time-Modulated Etching in a Dual-Frequency Capacitively Coupled Fluorocarbon Plasma, ***S. Jeong***, *D. Sung, K. Kim, A. Ushakov, M. Park, S. Cho, S. Kim, H. Park*, SAMSUNG ELECTRONICS, South Korea

Time-modulated etching process in a dual-frequency capacitively coupled fluorocarbon plasma has been investigated. In the pulsed-mode, etching rate non-uniformity decreased compared to the continuous-mode. The non-uniformity further decreased with lowering duty ratio. In addition, we find that more complex dissociation pattern in time-modulated fluorocarbon plasma than in continuous-wave driven plasma. Difference in the number of negative ions for the two different modes has been observed. We also discuss the relationship between the pulsed-mode process parameters and oxide-to-PR selectivities.

PS-ThP2 In-situ Plasma Diagnostics Study of a Commercial High Power Hollow Cathode Magnetron (HCM) Deposition Tool, ***R. Raju***, *L. Meng, H. Shin, D.N. Ruzic*, University of Illinois at Urbana-Champaign

The development of special plasma diagnostic techniques is required to characterize the plasmas used in physical vapor deposition (PVD) and plasma enhanced chemical vapor deposition (PECVD) commercial tools because of the intense deposition environment, non-standard geometry, and non-standard frequencies. A commercial 200mm INOVA high power (36 kW) HCM deposition tool with computer controlled system was set-up and used as a realistic PVD test bed for designing and testing the new plasma diagnostics techniques. A 3-D scanning RF compensated Langmuir probe was designed, constructed and used to get spatial information of plasma temperature and density in the HCM tool at various input power (0-15 kW), pressure (10-70 mTorr) ranges. Measured electron temperature values are in the range of 1-3 eV and the electron density is between 6×10^{10} to 2×10^{12} cm^{-3}. While operating the tool, deposition of metal on the tungsten probe tip and the insulator probe body was observed. In order to sputter away the deposited material from the tip of the probe a self-cleaning in-situ plasma cup was designed. The plasma cup has a side cleaning station so that RF compensated Langmuir probe can be moved into it, cleaned and return to its original condition without being withdrawn from the system. We observed a considerable variation in electron temperature and density values after the probe was exposed in a 2 kW metal plasma for about 10 minutes. After cleaning the probe tip for about 8 minutes we observed a recovery of electron temperature to the initial value, however the measured electron density was not recovered. Further results revealed the importance of other effects such as probe temperature, temperature of the tool and the probe surface condition. The conductivity of the probe body surface decreases with an increase in deposition time. Hence it is necessary to clean the probe body as well as the probe tip to get more reliable plasma parameter values. A new method to clean the probe body in-situ has been implemented and results will be presented. Further experiments have been conducted to find the deposition rates and ionization fraction of the incident metal atom species employing a quartz crystal microbalance combined with electrostatic filters. A full 3-D scan of parameters is presented.

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PS-ThP3 Optical and Electrical Diagnostics of an rf-Capacitively Coupled Plasma, ***H.W. Chang***, *C.C. Hsu*, National Taiwan University

Diagnostic studies of a low pressure rf capacitively coupled plasma in mixtures of Ar and O_2 were performed. This home-made plasma system has a cylindrical chamber with upper and lower annular electrodes; the electrode height can be adjusted. A voltage and a current probe were used to monitor the voltage and the current waveforms on the powered electrode with the focus of investigating the significance of the harmonics for plasma diagnostics. The amplitude, phase shift, and up-to-the 6^{th}-harmonics of the voltage and current waveforms were recorded. The optical emission of the plasma was monitored using an optical emission spectrometer. It is found in this work that the 3^{rd} and 4^{th} harmonics become more prominent in Ar-rich conditions and the waveform shows a significant distortion from the 13.56 MHz sinusoid. Upon changing the electrode positions, the current and voltage waveform amplitude as well as the optical emission intensities of multiple peaks show variations below 20%. The 3^{rd} and 4^{th} harmonics in the current waveforms show up-to-50% variations throughout the conditions investigated. This suggests that the harmonic is a more sensitive measure for plasma monitoring. The correlation between operation conditions and diagnostic measurements will be established. The implication of the waveform harmonics to plasma processes will also be discussed.

PS-ThP4 Characterization of Dual Frequency Capacitively-Coupled Oxygen Plasmas by Trace Rare Gases–optical Emission Spectroscopy (TRG-OES), ***Z. Chen***, *V.M. Donnelly, D.J. Economou*, University of Houston, *L. Chen, M. Funk, R. Sundararajan*, Tokyo Electron America, Inc.

Oxygen-containing plasmas are widely used for etching of fine features in microelectronics manufacturing. Dual-frequency capacitively-coupled reactors offer some advantages over inductive plasmas. The determination of the neutral species density and electron temperature (T_e) as a function of radio frequency (RF) power(s) and pressure are important in the understanding and optimization of the plasma etching processes in these systems. In this study, trace rare gases–optical emission spectroscopy (TRG–OES) was used to measure T_e, in a dual frequency capacitively-coupled oxygen plasma sustained by a high frequency (60 MHz) "source" upper electrode, and a 13.56 MHz voltage applied to the wafer-supporting lower electrode. TRG-OES is a nonintrusive method for determining plasma electron temperature and, under some conditions, electron energy distributions. The method is based on a comparison of atomic emission intensities from trace amounts of rare gases (a mixture of He, Ne, Ar, Kr, and Xe) added to the plasma, with intensities calculated from a model. In the present experiments, a small amount (5%) of a mixture containing 40% Ne, 20% Ar, 20% Kr and 20% Xe was added to the O_2 feed gas. T_e was measured across the plasma at a height of 5 mm above the lower electrode as a function of pressure (2-200 mTorr) at different applied RF powers. Oxygen atom densities were estimated by O-atom optical emission (844.6 nm), and rare gas actinometry (Ar, 750.4 nm). Results illustrated that T_e in an O_2 plasma with 1000 W upper power and no lower electrode power varies inversely with pressure, from 6.8 eV at 2 mTorr to 3.5 eV at 200 mTorr. As power was increasingly applied to the lower electrode, T_e at low pressure (e.g. 2 mTorr) hardly changed while, at higher pressures, T_e increased to the point that at 500 W lower electrode power, T_e was nearly independent of pressure. Percent dissociations derived from O-atom densities were quite low (<5%), even at the highest upper electrode power.

PS-ThP5 Synthesis of Single-Walled Carbon Nanotubes by Oxygen-Assisted Plasma Enhanced Chemical Vapor Deposition, ***S.W. Huang***, *C.H. Hsiao, K.-C. Leou, C.-H. Tsai*, National Tsing Hua University, Taiwan

Single-walled carbon nanotubes (SWNTs) have attracted a great deal of attention recently due to their unique physical properties and a wide range of potential applications, in particular, field effect transistors (FET) and nano-photonic devices. It is highly desirable to develop a method compatible with standard semiconductor microfabrication processes for direct synthesis of high quality SWNTs. In this work, we demonstrated a low temperature growth process of SWNTs on silicon substrates by inductively coupled plasma chemical vapor deposition (ICP-CVD) method with CH_4/H_2 gas mixture as base processing gases. A unique $Ni/Al/SiO_2$ nanocatalysts/support system has also been developed to allow the growth of high quality SWNTs. To further improve the crystalline structure of SWNTs, oxygen was added to the processing gas mixture to remove amorphous carbons during the growth process. Both the scanning electron microscopy and micro-Raman spectra were employed for characterizations of the SWNTs. The SWNTs were successfully synthesized at a temperature as low as 600°C. Parametric experiments were conducted to optimize the O_2 fraction in the gas mixture. Experimental results show that a low fraction of Oxygen not only increases the growth rate of SWNTs but also improve the quality of the tubes. The SWNTs are damaged, however, if the fraction of oxygen is too high.

PS-ThP6 Characterization of Platinum Catalyst Supported on Carbon Nanoballs Prepared by Solution Plasma Processing, ***Y. Ichino***, *K. Mitamura, N. Saito, O. Takai*, Nagoya University, Japan

Nonequilibrium plasma in aqueous solution, which is solution plasma (SP), is expected as a frontier of plasma nanomaterials processing. The SP processing can realize rapid synthesis at low temperature compared to the conventional methods such as chemical synthesis in solution and plasma processing in gas. We had successfully synthesized Au, Pt and FePt nanoparticles by SP processing. On the other hand, carbon nanoball (CNB) is one of carbon nanomaterial such as carbon nanotube (CNT) and fullerene. The CNB is expected as an electrode material for fuel cells. We already have been successful to synthesis well-defined CNBs. In order to improve the energy-conversion efficiency in fuel cells, Pt nanoparticles must be mounted on CNBs in the high density. In this study, we aim to prepare Pt nanoparticles in the high density supported on CNB (Pt/CNB) by using SP processing and to characterize the properties as the electrode for fuel cells. Carbon nanoball was prepared by thermal CVD process. Ethylene was used

as a raw material. Argon and hydrogen ware used as carrier gases. Solution plasma was generated by a pulsed power supply. Tungsten wire coated with alumina was used as the electrodes. 1.44 mM H_2PtCl_6 solution was added to 50 mg CNB, and polyvinylpyrrolidone (PVP) or sodium dodecyl sulfate (SDS) as a protective agent. After the discharge, the obtained Pt/CNBs were characterized by a scanning transmission electron microscope (STEM), energy dispersive X-ray spectroscopy (EDS) inductively-coupled plasma optical emission spectrometry (ICP-OES). The catalytic properties of Pt/CNB was evaluated by cyclic voltammetry (CV). Color of the solution changed from yellow to dark brown as synthesis time. This change indicates the decrease of H_2PtCl_6 complex in the solution and the improvement of dispersibility of CNB. Moreover, STEM images and elemental mapping images show the Pt nanoparticles supported on CNB. A catalytic activity of the obtained Pt/CNB was shown to be higher than the Pt/CNB prepared by conventional method since the adsorption wave of hydrogen was observed from CV. The activity was varied by the amount of supported Pt nanoparticles, which depended on SP processing conditions.

PS-ThP7 Effect of Dissolved Gases and Ions onto Solution Plasma Fields, ***N. Fujikawa***, *N. Saito, O. Takai*, Nagoya University, Japan

Solution Plasma (SP) is defined as a nonequilibrium discharge phenomenon in liquid solution. The higher reaction rate is expected since it supplies UV light, electrons, and radicals to liquid phase. SP processing is one of attractive reaction field for nano materials synthesis. However, there are few reports on solution plasma processing, in particular, fundamental research. We had been successful to fabricate various nanoparticles such as Au, Pt, FePt, In_2O_3 by SP processing. The reaction mechanism in the solution plasma has not been understood in detail. Reduction must be mainly occurred on these syntheses. However, oxygen and oxygen radical also be produced in the solution plasma. Why does not oxidation proceed? There are many other questions in SP processing. In this study, we aimed to investigate influences of dissolved substance, eg. O_2, ions on the reactive species in the solution plasma. A pulsed power supply was utilized to generate plasma. Needle-shaped tungsten (diameter: 1 mm) was utilized as an electrode. Voltage between electrodes, pulse width and frequency were 2400V, 2μs and 15kHz, respectively. Optical emission spectra were measured with a emission spectrophotometer. Ar or O_2 gases were introduced into the solution in order to vary the amount of dissolved oxygen. Discharge time was 30min. and solution temperature was varied from 10 to 30°C. Moreover, several kinds of chlorides were added into liquid solution in order to observed influences of ions. Peaks attributed to H_α, H_β, H_γ and O were observed in optical emission spectra. The presence originated from decomposition of water. The each intensity is almost constant although the flow rates of O_2 and Ar gases varied. From this, dissolved oxygen did not have a great effect on plasma state. On the other hand, peaks attributed to cation produced from chlorides were observed although peaks of chlorine were not observed. These differences would be discussed from the viewpoint of mobility in the solution, molecular weight, molecular or ion radius, and the reactivity of activated species.

PS-ThP8 Organic Compounds Synthesized by Short-Pulsed Discharge in Aqueous Solution, ***T. Mori***, *K. Mitamura, N. Saito, O. Takai*, Nagoya University, Japan

Some scientists had attempted amino-acid synthesis in order to represent origin of livings. For example, S.L.Miller obtained amino-acid after generating cyanide and aldehyde from discharged mixture gas, which consisted of NH_3, CH_4, H_2 and H_2O. This gas is main composition in primitive atmosphere in ancient times. Recently, we had been successful to generate solution plasma, which is one of pulsed discharge phenomenon in the solution. This is nonequilibrium plasma in solution. Thus, we can form cold plasma in the solution. Solution plasma supply many amount of radicals, ions and electrons, and intensive ultraviolet even at room temperature. Such state might be found on the earth, in particular, near seawater surface. In this study, we attempted to synthesize amino-acid by using the solution plasma in C-H-O-N solution system. As first experiments, organic synthesis with solution plasma was conducted in methanol and water system. Solution plasma was generated by using a short-pulsed power supply. After discharge, the ninhydrin solution was added to the obtained solution in order to confirm the formation of amino-acid through ninhydrin reaction. When amino-acid is produced, the color of the solution changes into Ruhemann's purple. Moreover the product in the solution was analyzed by nuclear magnetic resonance (NMR). While the ratio of methanol to water was varied, the amount of products and their species were investigated in detail. Solution plasma was generated in solution consisting of ethanol and water. Formation of acetaldehyde in the solution was confirmed by silver-mirror reaction and NMR analysis. Formation of CH_4, H_2 and O_2 gases was also confirmed by gas chromatography. The gases might be produced via several recombination reaction between radicals in the solution plasma. Additionally, while the ratio of ethanol to water was varied, the generation amount of CH_4 and H_2 changed drastically. The variation of ratio has a great influence on excited state and the reaction in the solution plasma. The productants synthesized in other solutions were discussed as same manner.

PS-ThP9 Excited Species by Shorter-Pulsed Electrical Discharges in Aqueous Solutions: Effect of Electrodes with Low Work Function, ***C. Miron***, *M.A. Bratescu, N. Saito, O. Takai*, Nagoya University, Japan

Pulsed electrical discharges in water have shown to produce hydrogen, ozone, oxygen, hydroxyl radicals and other chemically active species, making these techniques useful for several applications, such as water purification, nanoparticles synthesis. The electrical discharges in liquids were realized using different types of electrodes, such as copper, tungsten, stainless steel. During the experimental work many difficulties have been encountered due to the sparks and electrodes erosion process. Electrodes of high melting point, corrosion-resistant and high stability are required in realizing the electrical discharges in liquids. The objective of the present work is to investigate the optical properties of a pulsed glow discharge in ultrapure water between two electrodes with low work function, such as lanthanum hexaboride and tungsten. The effect of the electrode material on some physicochemical processes generated in solution plasma was realized by using time-resolved optical spectroscopy technique. Lanthanum hexaboride (LaB6) cathode has high stability and a very low work function (2.5 eV) in high vacuum, which changes when temperature is increased. Also is an excellent electron emitter material due to the oxygen adsorption on the lanthanum sites. The lifetime of these cathodes is 10 – 15 times longer than that of the tungsten cathodes. The behavior of the plasma and some properties of the LaB6 and tungsten electrodes, their effects on the time evolution of the reactive species generated in the electrical discharges in water were investigated in the present work. Time-resolved optical spectroscopy of the reactive species generated in the plasma showed a different evolution in time, depending on the electrode material, the life time of the excited species, and pulse polarity of the applied pulsed voltage. The electron temperature in the plasma was very low when LaB6 electrodes were used in the process, compared to the electron temperature obtained in the atmospheric pressure air plasmas. The low value of the electron temperature explains the broad band spectrum of the molecular species acquired in the electrical discharges generated in ultrapure water.

PS-ThP10 Effects of Vacuum-Ultraviolet Radiation on the Plasma-Induced Charging of Patterned-Dielectric Materials, ***G.S. Upadhyaya***, *J.L. Shohet*, University of Wisconsin-Madison

In this work, the effects of vacuum-ultraviolet (VUV) radiation on plasma-induced charging of patterned-dielectric structures are investigated. Experimental results show that supplemental-VUV radiation exposure of patterned dielectrics is beneficial in minimizing the plasma-induced charge on patterned-dielectric structures. The results of this work indicate that exposure of patterned-dielectric materials to VUV radiation during plasma processing can be useful in reducing or eliminating structural and electrical damage caused to patterned dielectrics by electron shading. Investigation of the effects of VUV radiation on the plasma charging of dielectrics was accomplished by evaluating the response of unpatterned, plasma-charged, oxide-coated samples exposed to monochromatic-synchrotron-VUV radiation at the University of Wisconsin-Synchrotron Radiation Center. VUV exposure of unpatterned SiO2/Si wafers indicated that photon energies less than or equal to 11 eV are beneficial in depleting the plasma-induced charge. The radiation-response experiments were subsequently extended to include patterned-dielectric wafers. Specialized, patterned-test structures with different aspect ratios (depth/width of a pit) were charged in a DC plasma and subsequently exposed to monochromatic-synchrotron-VUV radiation. Surface-potential measurements revealed significant charge depletion for photon energies in the range from 8-11 eV thereby indicating the beneficial effect of VUV radiation during plasma processing of patterned dielectrics. In addition, it was observed that the number of photons required to deplete charge in patterned dielectrics increases with the increasing aspect ratio of the pits in the patterned wafer. The experimental results are explained with equivalent-circuit models which suggest that electron photoinjection from the Si substrate as well as oxide surface conductivity play an important role in depleting the plasma-induced charge on the patterned-dielectric materials. Thus, we conclude that plasma-charging-induced damage in patterned-dielectric materials can be minimized by supplemental VUV exposure of the wafers during plasma processing.

Work supported by NSF under Grant DMR-0306582 and in part by the Semiconductor Research Corporation under Contract 2008-KJ-1781. The UW Synchrotron is a National Facility supported by NSF under Grant DMR-0084402. *G.S. Upadhyaya present address: Lam Research Corp., Fremont CA. .

PS-ThP11 How Far Should Be for Being Remote Plasma?, ***Y. Kim***, *W.K. Yang, J.H. Joo*, Kunsan National University, Korea

Remote plasma has been used in PEALD to reduce adsorbed precursor into a compound layer like HfO_2. The demanding role of plasma is a supplier of radicals not ions which might induce charge damage to devices. We focused the effects of plasma in two aspects; ion transport and thermal energy transfer to the wafer which have been underestimated in previous works. Advanced Energy's Remote Plasma Source is installed 300mm above a wafer and operated at a few to hundreds of mTorr range, within 1.5kW. Plasma was well localized within the quartz chamber region at high pressure regime due to reduced mobility of charged particles. At 10mTorr, plasma was spread to all over the chamber. Measured surface temperatures at four points from the wafer showed 50, 70, 150, and 600°C within a minute from ignition of Ar ICP(~2MHz, 500W). Temperature rise at the wafer surface could be from three mechanisms: ion kinetic energy, ion and meta-stable recombination heat release. We developed a 2D and 3D fluid based model using CFD-ACE+ to investigate heat transfer from plasma source including chamber outside cooling by air.

PS-ThP12 Real Time Feedback Control of Plasma Density by using a Floating Probe in Inductively Coupled Plasmas, ***S.H. Jang***, *M.H. Lee, C.W. Chung*, Hanyang University, Republic of Korea

A real time feedback control of plasma density to apply processing plasmas was carried out experimentally in inductively coupled plasma (ICP). The plasma density control can contribute good processing performance because etched and deposition rate are generally a function of the plasma density, and it influences other processing parameters such as the number of radicals, uniformity, processing time etc. In this study, the plasma density was measured by a floating probe which can measure the plasma density in real time without plasma perturbation installed as a sensor on a chamber wall, and the measured information was fed back to actuator to influence the plasma density. This plasma control system allowed the plasma density to reach and keep the desired densities below 0.1% of the state error. To describe External disturbances, the pressure of the chamber was dropped from 10 mTorr to 5 mTorr by using a molecular flow controller. At the pressure disturbance, the density decreases, and recovers with 1.5% of the maximum error and 10 s of the settling time. In the comparison of active and inactive control with pressure disturbance, the Maximum state errors were 1.5% and 40% respectively.

PS-ThP13 Time Resolved Measurements of the Electron Density with a Cutoff Probe in a Pulsed Plasma, ***J.-H. Kim***, *S.J. You*, Korea Research Institute of Standards and Science, *B.-K. Na*, Korea Advanced Institute of Science and Technology, *D.-J. Seong, Y.-H. Shin*, Korea Research Institute of Standards and Science

In pulse-modulated capacitively coupled plasmas generated in Ar/CF4 mixtures, time variations of the electron density were measured with a cutoff probe. For measuring the cutoff frequency, a microwave is introduced through a radiating antenna to the plasma, and the transmitted wave is detected on a receiving antenna connected to a port of an oscilloscope. From the transmission spectrum we obtained the wave cutoff frequency, which could directly give the electron density. To measure the time variation of cutoff frequency, we scanned the transmitted signal with time for a fixed frequency, which was done for next fixed frequency and so on. Thus, we accumulated the time variations of the transmitted signal data for each different frequency and transposed the data array. Therefore, we obtained the time variation of the cutoff frequency. We investigated the decay time of the electron density for different pressures, repetition frequencies of the pulse modulation, and duty ratios.

Authors Index

Bold page numbers indicate the presenter