Characteristics of discharge microplasmas generated in highly fluctuating fluids and their application to the synthesis of molecular diamond

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Plasma-based fabrication of novel nanomaterials and nanostructures is paramount for the development of next-generation electronic devices and green energy. In particular, controlling the interactions between plasmas and materials interfaces, and the plasma fluctuations are crucial for further development of plasma-based processes and bottom-up growth of nanomaterials. Discharge microplasmas generated in supercritical fluids represent a special class of high-pressure plasmas where fluctuations on the molecular scale influence the discharge properties and the possible bottom-up growth of nanomaterials. In this talk, we will give an overview of the fundamental characteristics of discharge plasmas generated at high-pressure and supercritical conditions. In the second part of the presentation, the application of discharge plasmas generated in supercritical fluids for the synthesis of nanomaterials, especially nanodiamonds and molecular diamonds, so-called diamondoids, will be presented.

1. Characteristics of microplasma discharges generated in highly fluctuating media

Supercritical fluids (SCFs) are media above the critical point that possess properties intermediate between those of gases and liquids. Their main characteristics are high diffusivity, high dissolving power, and low surface tension, which can be changed continuously by modifying pressure and/or temperature. Discharge plasmas generated in such media allow combining the superior transport properties of SCFs with the high reactivity of plasmas, which makes them interesting for the synthesis of novel nanomaterials.

For discharges whose characteristic dimension is on the order of a few microns, it has been discovered that they exhibit an anomaly near the critical point, a local decrease in the breakdown voltage, which has been observed for both molecular and monoatomic gases [1-4]. This anomalous behavior is caused by the concomitant decrease of the ionization potential due to the formation of clusters near the critical point, and the formation of extended electron mean free paths caused by the high-density fluctuation near the critical point. We also show that for microplasmas, the characteristic of the SCF, i.e. the high-density fluctuation near the critical point, persists [5].

2. Application of discharge plasmas generated in supercritical fluids to the synthesis of diamondoids

Diamondoids are a series of sp³-hybridized carbon allotropes that stand apart from other carbon nanomaterials (fullerenes, carbon nanotubes, and graphenes), which are sp²-hybridized [6]. Unlike nanodiamonds, diamondoids possess well-defined surface terminations and molecular structures, and they show promise for a wide range of applications in biotechnology, medicine, and opto- and nanoelectronics. However, larger diamondoids are difficult to obtain by conventional organic synthesis methods due to the exponential increase of possible reaction intermediates and reaction pathways.

Recently, we have shown that nanodiamonds and diamondoids can be synthesized by discharge plasmas generated in supercritical xenon [7], using the smallest diamondoid, adamantane, as a precursor and seed.

In this talk, we will present the synthesis of diamondoids both by batch-type [8] and continuous flow microreactors [9], and their characterization by micro-Raman and gas chromatography – mass spectrometry. Finally, we show that one possible growth mechanism of larger diamondoids from adamantane consists in the repeated abstraction of hydrogen terminations and the addition of methyl radicals [10].

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References

Spatio-temporal behavior of electric double layer, which exists at plasma-liquid nano-interface, is discussed on the basis of simultaneous numerical simulation of gas- and liquid phase in plasma in contact with liquid. Simulation results suggest that slow liquid ions preferentially interact with gas-phase species. Effects of size and arrangement of bubble plasmas and their fluctuation in liquid are also discussed by means of numerical simulation.

1. Introduction
Plasmas in liquid have attracted much attention because of their potential applications such as materials syntheses, treatments, and also medical treatments of living tissues [1-4]. In the material processing using plasma in liquid, the most important part sequence is the reactions at the plasma-liquid nano-interface. Such nano-interface exists at the surface of bubbles, in which plasma is generated. In addition, the size and arrangement of the bubbles are spatially and temporally fluctuating in liquid. In this paper, I would like to discuss how the plasma-liquid nano-interface and its fluctuation affect the final results of material processing using plasma in liquid using numerical simulation.

2. Plasma-Liquid Nano-Interface
From the viewpoint of electrochemistry, plasma in contact with liquid surface works as an electrode. In the liquid in contact with the electrode, nano-scale electric double layer (EDL) is known to be formed. The EDL is a kind of sheath in plasma, which is governed by behavior of space charges near the electrode. According to our previous study, slow liquid ions tend to be left on the top surface of liquid in contact with plasma when the plasma is generated by ac-driven DBD as shown in Fig. 1. Although experimental proofs are not available yet, this tendency implies that slow liquid ions preferentially interact with the species supplied from gas-phase plasma, and govern reactions to generate final products in liquid.

3. Effects of Size and Arrangement of Bubbles
Effects of size and arrangement of bubbles in water was examined in flow reactor. Figure 2 shows effects of bubble arrangement on the rate of liquid products through a flow reactor. As can be easily expected, there is a set of optimum size and distance of the bubbles for obtaining maximum production rate. In the symposium, I would like to discuss the effects of fluctuation of the arrangement of the bubbles on the efficiency of liquid treatment.

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References

Fig. 1 Concentration of fast positive ions X and slow negative ions Y on the top surface of liquid in contact with Ar-DBD.

Fig. 2 Effects of size and number of bubbles on liquid treatment efficiency in a flow-reactor.
Plasma-liquid interaction of atmospheric DC glow discharge using liquid electrode for synthesis of metal nanoparticles

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For the synthesis of metal nanoparticles in aqueous solution, we propose dual plasma electrolysis, which consists of Hoffman electrolysis apparatus with two atmospheric glow discharge plasmas as electrodes instead of conventional metal electrodes immersed in a liquid. The plasma anode irradiates positive ions to the solution surface while the plasma cathode irradiates electrons to the solution surface. The dual plasma electrolysis system enables us simultaneously to investigate the influence of electron and positive ion irradiation to a solution surface on metal nanoparticle generation at the same current. In this work, we used aqueous solutions of AgNO₃, HAuCl₄ to dual plasma electrolysis for synthesis of metal nanoparticles. We investigated the dependence of nanoparticle size and shape on discharge gas and pH of the liquid.

1. Introduction

Non-thermal plasma in contact with liquids such as atmospheric DC plasma using liquid electrode has attracted considerable interest for its potential use in a wide range of applications[1]. When we focus on the liquid reaction, the plasma system is considered as electrolysis using a plasma electrode. The plasma electrode supplies electrons or ions into the liquid, generating different reactions from those observed in conventional electrolysis using metal electrodes. When metal cations are dissolved in a solution, metallic nanoparticles are synthesized at the liquid surface by electron or positive ion irradiation from the plasma. We tried to control the reaction of nanoparticle synthesis by changing the discharge parameters such as gases and pH of the liquid.

2. Experimental Results

Figure 1 shows the experimental setup of dual plasma electrolysis used for the synthesis of nanoparticles. In order to divide the anodic and cathodic reactions, we used an H-shaped glass vessel reactor known as the Hoffman electrolysis apparatus. The reactor is filled with an electrolyte of AgNO₃ solution with a concentration of 10⁻³ mol/l or HAuCl₄ solution with a concentration of 10⁻⁷ mol/l. By adding HCl or NaCl solution, pH value is controlled. The stainless-steel nozzle anode has an inner and outer diameters of 500 and 800 μm, respectively. The gap length is 1 mm. Helium is fed through the nozzle electrode in open air. The gas flow rate is adjusted 200 sccm using a mass flow controller. The glow discharge is generated by applying a dc voltage. To avoid influence of air existence, we use sheath flow system. Namely other gas (N₂ or O₂) flows around the helium flow. Using sheath flow system, redox reaction at the plasma-liquid interface can be controlled.

When helium flow plasma without sheath flow is used for plasma electrolysis with HAuCl₄, the color of the liquid on both the plasma anode and cathode sides becomes red. This red color results from the surface plasmon resonance of Au nanoparticles, and it indicates the generation of Au nanoparticles. The structure and size of the nanoparticles depend on the reaction rate. When nitrogen sheath flow plasma is used, many nanoparticles with triangle structure are generated in plasma anode side. When oxygen sheath flow plasma is used, nanoparticles become smaller in plasma cathode side. When pH of the liquid is changed, other reactions are occurred. For instance, in the case of using only AgNO₃ solution, only plasma cathode side becomes yellow color which originates from the surface plasmon resonance of Ag nanoparticles. That is, Ag nanoparticles are synthesized at the plasma-liquid interface. With HCl and AgNO₃ solution, the color of the liquid on both the plasma anode and cathode sides doesn’t change. That is, Ag nanoparticles are not synthesized at this condition. With NaOH and AgNO₃ solution, the color of the liquid on both the plasma anode and cathode sides becomes gray which indicate some particles are generated. The detail mechanisms are still unclear, we experimentally confirm that synthesis of metal nanoparticles by plasma-liquid interaction depend on discharge gas and pH of liquid.

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References

Control of cellular activities by oxygen radical treatment

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The budding yeast cells were exposed by the atmospheric-pressure oxygen radical source, which only produces neutral oxygen species. The effects of oxygen radical treatment on yeast cell growth changed from promotion to repression with increasing the dose of oxygen species.

1. Introduction
Various stimuli or stresses cause various responses of microorganisms, such as activation, functional depression, and cell death, depending on the dose or flux of factors. We have focused on the effects of neutral oxygen radicals on the inactivation of microorganisms using the atmospheric-pressure plasma or oxygen radical source.[1]-[7] We measured the absolute densities of ground-state oxygen atom(\(^3\)P), excited state oxygen molecule(\(^1\)\(\Delta\)), and ozone. We showed that ground-state atomic oxygen is the effective factor of inactivating \(P.\ digitatum\) spores and the oxidation of the spores were observed with fluorescence microscopy.

In this study, we investigated the effects of oxygen radicals on inactivation as well as promotion or repression of proliferation of budding yeast cells.

2. Experimental procedure
The budding yeast cells (\(Saccharomyces\ cerevisiae\ W303a\)) were suspended with phosphate buffered saline. The suspensions were treated with oxygen radicals using an atmospheric-pressure oxygen radical source, which only produces neutral species. The \(O_2/(Ar+O_3)\) flow rate ratio and total flow rate were 0.6% and 5 slm, respectively. The O and \(O_3\) densities were measured to be \(2.3\times10^{14}\) cm\(^{-3}\) and \(8.0\times10^{14}\) cm\(^{-3}\) at 10 mm from exit of the radical source using vacuum ultraviolet absorption spectroscopy, respectively. The radical source and the dish were enclosed with a plastic cover to eliminate the influence of ambient air. Recovered cells were arranged to be \(1.0\times10^6\) cells/ml, and cultured with yeast extract peptone dextrose (YPD) medium at 30\(^\circ\)C for 48 h. For the evaluation of yeast cell growth, we counted the number of cells.

3. Result
Figure 1 shows yeast cell growth as a function of treatment time. The vertical axis indicates the ratio of the number of survivors after the treatment to control cells. Cell growth was promoted from 10 to 20\% with the oxygen radical treatment between 30 and 90 s. On the other hand, cell growth was repressed about 10\% with the oxygen radical treatment between 120 and 180 s. These results suggested that the effects of oxygen radical treatment on yeast cell growth changed from promotion to repression with increasing the dose of oxygen radicals.

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References
Plasma-liquid interactions: from nano-colloids to bacteria-containing aerosols

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The interactions of atmospheric pressure plasmas with liquid samples have opened a range of new opportunities in diverse technological fields. At the same time, the research efforts have revealed interesting and challenging scientific questions on the behavior of hybrid plasma-liquid systems. In this contribution fundamental aspects of plasma-water interactions are reviewed and analyzed in some details for a given microplasma configuration [1]. These basic concepts will then be used to elucidate the mechanisms that lead to the synthesis and surface engineering of nanoparticles via microplasma-induced liquid chemistry [2-4]. The same basic concepts are also fundamental to understand the outcome of plasmas applied with biological fluids. Therefore plasma interactions with liquids that contain bacteria will be discussed in general; in more details the effects of charging phenomena are considered both theoretically as well as experimentally.

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References
Discharge Characteristics of Plasma Jet Operated in Gas-Mixture System for Plasma Biomedicine

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We present here discharge characteristics of dielectric-barrier-discharge plasma jet in the controlled He/N₂ gas-mixing system. The length of the plasma plume increases from 62 to 140 mm with increasing the discharge voltage from 6 to 10 kV, which is much longer than that of the plasma plume produced under the open-air condition. The stability of the plasma plume is sensitive to ambient N₂ flow condition, and the stable long plasma plume is realized in the controlled He/N₂ mixture system.

1. Introduction

Atmospheric pressure plasma jet has been widely employed in biomedical applications because such plasmas induce little thermal damage to biomaterials [1-6]. Especially dielectric-barrier-discharge (DBD) plasma jet, where the dielectric prevents the formation of the high temperature arcs, is the most common atmospheric pressure discharge system [7-24]. DBD non-equilibrium plasma has relatively high electron temperature and low gas temperature, and the high energy electrons can produce chemically rich gas-phase environments around room temperature. The atmospheric DBD plasma jet, which generally shows frame length as long as several cm, can be easily generated by the application of high voltage with low frequency electric pulses in open air. However, the control of chemical reactions in DBD plasma jet is quite difficult because the DBD discharge is transient, and the discharge is self-extinguished within about a few μsec after discharge initiation. Therefore, further experimental investigations are needed to realize the control of the transient discharge in plasma jet for biomedical applications. In this study, we report the discharge characteristics of the plasma plume in the controlled He/N₂ gas-mixture system.

2. Results and discussion

The DBD plasma jet was ignited in a quartz tube wrapped with copper metal strips of 45 and 15 wide as the power and ground electrode, respectively. He gas was fed through the quartz tube, and N₂ gas was supplied outside the tube reactor. The gas flow rate of He and N₂ was 3 and 10 slm, respectively. The power electrode was connected to 5 kHz positive pulse voltage with potentials from 6 to 10 kV. Figure 1 shows (a) the experimental setup for production of DBD plasma jet, and (b) photograph of the long plasma jet operated in He/N₂ gas mixture. The length of the plasma plume increases from 62 to 140 mm with increasing the discharge voltage from 6 to 10 kV, which is much longer than that of the plasma plume produced under the open-air condition. The stability of the plasma plume is sensitive to ambient N₂ flow condition, and the stable long plasma plume is realized in controlled He/N₂ mixture system.

Figure 2 shows the optical emission intensity of (a) N₂⁺ 391 nm and (b) He 706 nm, as a function of discharge voltage. N₂⁺ emission intensity decreases with increasing discharge voltage. The N₂⁺ emission intensity is closely related to the number density of He metastable atoms He(2³S), because He(2³S) density decays via the Penning ionization reaction of N₂ molecules, resulting in the production of N₂⁺ ions in He/N₂ mixing system. The effects of gas-mixing structure on discharge characteristics is discussed in this study.

Fig. 1. (a) Experimental apparatus of DBD plasma jet. (b) Photograph of the long plasma jet operated in He/N₂ gas mixture.
Fig. 2. Discharge voltage dependence of emission spectrum intensity of (a) N$_2^+$ 391 nm and (b) He 706 nm. He and N$_2$ gas flow rate is 3 and 10 slm, respectively.

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References

Electron Spin Resonance Analyses of Plasma-Biological Material Interactions in Atmospheric Pressure Plasmas

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Mechanisms of plasma-surface interaction are required to understand in order to control the reactions precisely. Recent progress in atmospheric pressure plasma provides to apply as a tool of medical treatments. To use the plasma with safety and optimization, the real time in situ detection of free radicals - in particular dangling bonds - by using the electron-spin resonance (ESR) technique is one method which has been developed, because the free radical plays important roles for dominantly biological reactions.

1. Introduction
Nonequilibrium atmospheric pressure plasmas (NEAPP) have feasibly applied blood coagulation by Fridman et al.[1] They discussed about the suggestive coagulation mechanism involving phospholipid radicals reaction with peroxides and polymerization to form fibrinogen converted from fibrin monomer.[1] Ikehara et al. reported that plasma treatments applied recently for blood coagulation during a surgical procedure and provided faster coagulation of the blood bleeding than natural hemostasis.[2] However, coagulation mechanisms have not clarified yet.

The NEAPP has effects on formation of intracellular reactive oxygen species (ROS) and most likely induction of organic peroxides in cell medium reported by Kalghatgi et al.[3] Similarly Iseki et al. reported preliminarily that the NEAPP treatments killed the human ovarian cancer cell lines.[4] Very recently, the NEAPP therapy has been focused on as a novel medical practice on the basis of effects of indirect NEAPP-activated medium (PAM) exposure on cell viability and tumor growth.[5,6] However, chemical changes in the PAM have not analyzed so far.

Hence the plasma-biological materials interactions are required to study for understanding effects of the NEAPP plasma treatments. Here we focused on the blood and cells as examples for biological materials and on any mechanism on the basis of chemical changes through radical formations. For detection of radicals, we applied in this study the real time in situ electron spin resonance (ESR) method, developed by our group.[7]

In this study, we have focused on detection of radicals on the biologically related specimen such as bloods and culture media before and after the NEAPP treatments.

2. Experimental
Samples of bloods and culture media were irradiated by the NEAPP treatments employed by our developed apparatus. The liquid samples were set in the ESR cavity and measured by the X-band ESR spectrometer.

After the plasma treatment of bloods, ESR signals were observed clearly. The signal has not identified yet but a candidate for heme b in bloods. Figure 1 shows a temporal change of intensities for ESR signal arisen from free radicals generated by plasma treatments. As the APP treatment time increased, intensities of ESR signal were increased and saturated as the time exceeds 5 min. Preliminarily, we speculate that gaseous active species such as O atom and oxidative radicals may cause to the chemical changes on peptides and proteins of cells and tissues.

Furthermore, we will discuss about chemical changes through radical generations in the plasma-activated medium.

![Fig. 1 Temporal change of ESR spectral intensities for free radicals taken after the plasma treatments.](image)

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References
Diagnostics of activated species generated by AC excited non-equilibrium atmospheric pressure Ar plasma jet for plasma medical and bio applications

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The densities of the ground state O and N atom and the nitric oxide (NO) generated by AC power excited non-equilibrium atmospheric pressure Ar plasma jet (NEAPPJ) were measured by vacuum ultraviolet absorption spectroscopy (VUVAS) and laser induced fluorescence (LIF) spectroscopy, respectively. Up to the plasma jet region, the NO density increased with increasing the distance from plasma head, and then saturated in the remote region of plasma jet. On the other hand, the O atom density decreased from $10^{14}$ to $10^{13}$ cm$^{-3}$ with increasing the distance and N atom density increased at the remote region of plasma jet. These results are very important for understanding the bio and medical applications of NEAPPJ.

1. Introduction
Medical and bio applications of non-equilibrium plasma have been attracted much attention.[1,2] In these applications, NEAPPJ are frequently used, and the samples are typically located at the plasma remote region further from a main discharge. At an atmospheric pressure, the activated species frequently react with other species in the gas-phase because of high collision frequency. In the condition, the reactions between the plasmas and the samples are very complex and it is very difficult to understand the mechanism. Therefore, it is required to diagnose the behaviors of activated species generated by plasma discharge and to clarify the gas-phase reactions. In this study, behaviors of activated species generated by the NEAPPJ in open air have been measured by spectroscopic methods.

2. Experimental setup
The Ar NEAPPJ was generated between two metal electrode tips, to which a 60 Hz alternating voltage was applied, under the Ar gas flow rate of 2 slm. The distance between the electrodes was approximately 20 mm. The AC power supply provided a peak-to-peak voltage of around 18.0 kV (20 mA). A plasma jet was generated along the gas flow direction with a length of about 8 mm from a gas outlet slit. The absolute densities of O and N atoms in ground state were measured using VUVAS.[3,4] To measure the spatial distribution of O and N atom densities, the plasma source was moved along the direction of the gas stream, keeping the VUVAS measurement point. On the other hand, density of the nitric oxide (NO) was measured by using LIF spectroscopy with OPO laser and UV spectrometer with ICCD camera. The wavelength of laser light for the excitation of NO was 226.3 nm. The fluorescence was observed on A-X band with a bandpass filter (239±10 nm).

3. Results and discussions
Figure 1 shows absolute O and N atom densities and relative NO density as a function of the distance from the plasma head. The O atom density decreased from $10^{14}$ to $10^{13}$ cm$^{-3}$ with increasing the distance. N atom density was almost constant around $2 \times 10^{13}$ cm$^{-3}$ up to 10 mm and then increased. On the other hand, NO density increased with increasing the distance, and then saturated over 10 mm distance. In the plasma region, it is considered that O and N atoms are generated by dissociation of engulfed ambient air and other activated species such as excited nitrogen or oxygen are also generated by the air engulfment in the plasma jet, and the reactions between these species produce the nitrogen oxide species. Those molecular species are relatively stable compared with atomic species, therefore, transported to the plasma remote region by gas flow. Therefore, NO density increased with increasing the distance and was saturated in the plasma remote region. In the remote region, it is considered that O atom density decreased by the recombination processes, however, the N atom density increased by reactions between the nitrogen oxides and other excited species.[5]

Fig. 1 Densities of O (1P), N (1S) atoms, and NO as a function of the distance from the plasma head.

References
Dispersion and Waves in Bounded Plasmas with Subwavelength Inhomogeneities: Focused Ion Beams for Plasma Nanotechnology

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Bounded plasma exhibit many interesting properties that are not found in plasmas of “infinite” extent such as space and astrophysical plasmas. Our studies have revealed that the dispersion properties of waves in a bounded magnetoplasma deviates considerably from the predictions of the Clemmow-Mullaly-Allis (CMA) model, giving rise to new regimes of wave propagation and absorption. This article highlights some of these interesting effects observed in experiments. One of the principal outcomes of this research is the genesis of a novel multielement focused ion beam (MEFIB) system that utilizes compact bounded plasmas in a minimum – B field to provide intense focused ion beams of a variety of elements for plasma-based nanotechnology.

1. Introduction

Wave interaction with plasmas has been one of the most actively researched areas in plasma physics. Most of the earlier investigations focused on waves that have wavelengths much smaller compared to the size of the plasma and were on parallel wave propagation such as in large mirror devices. The wave phenomena in such large dimension plasmas were described by plane waves in the infinite and cold plasma approximation. Ideal cases of these “unbounded” plasmas include ionospheric and astrophysical plasmas that extend from tens to hundreds of kilometers. On the other hand bounded plasmas refer to small scale laboratory plasmas, where the plasma dimensions can vary from a few mm to several centimeters, and boundaries play an important role in dictating wave interaction with plasmas in such situations. Of special interest are plasmas where the plasma size is comparable or smaller than the wavelength of the waves. Moreover, if the length scales of nonuniformities and inhomogeneities in the plasma become comparable or smaller than the free space wavelength \( \lambda_{ow} \), the interaction becomes all the more interesting and new effects can be observed. Such wave generated compact plasmas belong to the subject of the present research.

2. Theoretical background

We at first look at plane wave dispersion in unbounded plasma in the infinite and cold plasma \( (T_i \cong T_e \to 0) \) approximation, for waves launched in the \( k \perp B \) mode. In the presence of a microwave electric field two cases can arise depending upon the polarization of the electric field with respect to \( B \), namely the ordinary \( E \parallel B \) (O-mode) and the extraordinary \( E \perp B \) (X-mode) modes of wave propagation. The dispersion relations are:

\[
\alpha_p = k_\alpha \sqrt{1 - \left( \alpha_p^2 / \omega_p \right)^2}, \quad \text{and} \quad \beta_k = \omega / \omega_p, \quad \text{where} \quad \alpha_p = \omega_p / \omega, \quad U = 1 + j(\omega_{\text{coll}} / \omega) \quad \text{and} \quad \beta_k = \omega / \omega_p, \quad \alpha_p = eB/m_e, \quad \text{and} \quad \omega \text{ are the angular, electron cyclotron, electron plasma, collision, and wave frequencies respectively. The dispersion is well represented by Clemmow-Mullaly-Allis (CMA) diagrams.}

An important outcome of the CMA model is that it becomes impossible to sustain waves in the high density \( (\alpha_p > 1) \) and low magnetic field \( (\beta_k < 1) \) limit.

The objective of the research is to investigate, when the boundaries are comparable to the free space wavelength of the waves, in a plasma confined in a minimum-B magnetic field, would the domains of wave propagation as predicted by the CMA model remain valid ?. The experimental results incorporate the warm plasma effects inherently. The results indicate an interesting possibility that in the presence of boundaries, wave propagation is possible through regimes considered prohibited by the existing cold plasma theory. This useful result has led to the development of miniature supercritical collimated plasmas for generation of multielement focused ion beams for nanotechnology.

3. Experiment

A schematic of the experimental system is shown in Fig. 1 with the details of the system and diagnostics provided in reference 1.

Fig. 1. Schematic of the experimental system. GC: guiding cylinder, QW: quartz window, SS: straight section, TST: stub tuner, DC: directional coupler, ISO: isolator, MWG: microwave generator, PSC: power supply, WS: Wilson seal, LP: Langmuir probe,

The system consists of a vacuum chamber VC having length of 50 cm and diameter of 20 cm, with four cylindrical arms having numerous ports for pumping, gas inlet, vacuum gauges, and plasma diagnostics. Argon and Krypton are used as experimental gases. The plasma is confined in a multicusp (MC) magnetic field with a thin metallic cylinder of inner radius $a = 41$ mm inserted inside MC to provide a uniform conducting boundary. Microwaves of 2.45 GHz is used for plasma generation. Langmuir probes are used for plasma diagnostics. The probes for wave electric and magnetic field measurements comprises of a spherical antenna probe and a B-dot probe to measure the wave B field. The experiments are performed at wave input power range $P_{in} = 180 – 540$ W and in the pressure range $p = 0.20 – 0.60$ mTorr.

4. Experimental results

The radial variation of the plasma electron temperature $T_e$ and ion density $N_i$ are shown in Fig. 2. The figure shows that $N_i$ has a maximum value at the center of MC and decreases towards the wall.

The density is supercritical for $r < 3$ cm (cutoff density $N_c = 7.44 \times 10^{10}$ cm$^{-3}$ for waves of 2.45 GHz) and $T_e$ is peaked in the resonance region ($\sim 1.7 - 2.5$ cm) and falls off on either sides. In the MC, the magnetic field is zero at the center and has a small value over a radius of 1 cm ($\beta_c \sim 10^{-4}$). Measurements of the wave electric field have shown finite penetration of waves through the central supercritical ($\alpha_c > 1$, $\beta_c < 1$) plasma [1]. Therefore boundaries do play an important role in modifying wave dispersion.

Ions have been extracted from these collimated plasmas for the generation of multielement focused ion beams (FIB) [2]. It is expected that the applicability and limitations of conventional Ga FIB systems can be overcome by having focused ion beams of a variety of gaseous atoms. Figure 3 shows the ion energy distribution measured by an ion energy analyzer at the plasma meniscus near the extraction region. The energy spread of the extracted ions is ~$5$ eV which is comparable to that of a LMIS (Liquid Metal Ion Source) based FIB [15].

![I-V characteristics for Argon plasma using an ion energy analyzer and the ion energy spread.](image1)

Fig. 3: I-V characteristics for Ar and Kr ion beams.

We next carried out experiments to investigate time dependent current profile during focused ion beam milling of a 10 µm free hanging Al metallic film. Argon and krypton ion beams of energies ~4 - 18 keV are employed and the beam current is recorded in real time as shown in Fig. 4.

![Variation of normalized collector current with time for Ar and Kr ion beams.](image2)

Fig. 4: Variation of normalized collector current with time for Ar and Kr ion beams.

It is observed that initially the ion current ($I_c$) is zero and after some time when the beam starts penetrating the film $I_c$ increases slowly with time and eventually tends to saturate. The threshold penetration time is typically ~50-100 seconds for Argon beams of ~0.8 µA. It may be noted that Kr ion beam requires a longer time than Ar. This would be related to the mass of the ionic species and the current associated with the beam.

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References

Analysis of DNA damage and cellular responses induced by atmospheric pressure plasma jet exposure

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Recently, non-thermal atmospheric pressure plasma has been studied in biological and medical applications. Among them, reactive oxygen species (ROS) in water injected by the plasma exposure play an important role. Therefore, we have been trying to use large DNA molecules as a biomarker to estimate intensity of the ROS in aqueous media. Here, we report the measurement of ROS by electron spin resonance (ESR) spectroscopy with spin trapping technique. The correlation between the signal intensity of OH radical measured by ESR and the number of strand breaks obtained by single-molecule DNA observation was examined. Furthermore, cellular responses in human cancer cells were also studied.

1. Introduction

Biological and medical applications of non-thermal plasma (NTP) have been widely studied. Especially an atmospheric pressure plasma jet (APPJ) is widely used because it can treat subjects without thermal loading, and length of the plasma jet can be adjusted by flow condition of noble gas. It is generally considered that reactive oxygen species (ROS) play an important role in plasma medicine due to a higher oxidation potential. To elucidate the cellular responses induced by exposure to NTP, we focused on (1) identification and quantification of reactive chemical species in aqueous media, (2) damage to suspended biomacromolecules, and (3) cellular response of mammalian cells (viability and apoptosis induction).

2. Materials and Methods

An atmospheric pressure argon plasma jet was generated by dielectric barrier discharge using a pulse power supply.

In this study, we measured the intensity of ROS using electron spin resonance (ESR) spectroscopy. DMPO was used as a spin trap agent. DMPO solution located at the tip of APPJ was exposed for different time duration and discharge condition. After exposure, ESR signal was immediately measured.

To evaluate the effect of plasmas in molecular level, we have been trying to use large DNA molecules as a biomarker. By exposing DNA to the plasma, oxidative damage to DNA can be induced. A single-molecule-based evaluation method of double-strand break using large linear DNA molecules was used [1]. The number of plasma-induced strand break on large DNA molecules was determined using a simple mathematical model [1].

Cellular responses of mammalian cells were evaluated in vitro using HEK293 (human embryonic kidney cells) and H460 (lung cancer cells). Viability and apoptosis induction were tested.

3. Results and Discussion

Figure 1 shows a schematic overview and the typical results of three experiments. First, DMPO-OH ESR signal intensity was measured. DMPO-OH signals intensity (arbitrary units) were increased with exposure time and the applied voltage. Then the correlation between DMPO-OH signals intensity and the number of strand breaks obtained from single-molecule DNA measurement was examined. The signal intensity was highly correlated with the number of strand breaks. Furthermore, apoptosis induction in cancer cells was observed after the APPJ exposure under the same condition of the above two experiments.

4. Conclusion

We observed DMPO-OH spin adduct in the plasma-treated liquid. The correlation between DMPO-OH signal intensity and the number of strand breaks suggests that OH radical highly affects DNA damage. Our single-DNA-based analysis could be used in estimation of ROS intensity and apoptosis induction activity.

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References

High Efficiency and Low Damage Plasma Gene Transfection Using Micro-capillary Electrode

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We have developed spatio-temporally stabilized micro-plasma gene transfection method by employing micro-capillary tube having combined functions of the gas nozzle and the HV (high voltage) electrode with grounded counter electrode sandwiching a plastic dish in which cells and plasmids are filled. It is shown that the micro-plasma transfect plasmids into target cells with high transfection rate and high survivability simultaneously.

1. Introduction

The demands on a safe and damage-free gene transfection method is increasing. A unique virus-free gene-transfection method using plasma irradiation developed by some of us (Satoh et al.) [1], and we have been developing and the plasma source in order to improve the transfection rate and suppress damage to cells and DNAs. This method realizes high transfection rate over 60% and low damage (no damage) to COS7 cells and DNAs simultaneously [2,3]. In this study, as the first step to know the plasma transfection mechanism, the role of the counter electrode is experimentally investigated.

2. Experiments and Discussion

![Fig. 1. (left) A plasma of the HV capillary and the GND (grounded) plate electrodes and (right) A plasma with the GND (grounded) needle electrodes of 0.3 mm tip diameter.](image)

We have developed spatio-temporally stabilized micro-plasma irradiation system by employing small capillary tube having combined functions of the gas nozzle and the HV (high voltage) electrode with grounded counter electrode sandwiching a plastic petri dish in which cultured cells and plasmids are filled. Two different types of electrodes, cupper plate and metal needle (tip diameter is 0.3 mm), were investigated. Figure 1 shows the each plasma with these counter electrode respectively. Sinusoidal voltage of 20 kHz was applied on the capillary electrode, which was pulse-modulated at a repetitive frequency of 25–30 pps with a duty ratio of 1%. Typical conditions of the voltage and the current were 10–20 kV (pp: peak to peak) and 5–100 mA (pp) respectively. Helium gas was flowed inside the capillary tube with flow rate of 0–1 sccm. As shown in figure 1, plasma becomes narrow and the area cell destroyed is limited though the DNA transfection area is also limited as shown in Figure2. This result shows that plasma causes necrosis on the cells which is directly irradiated plasma, and that in the neighboring area DNA is transfected. This means some particular charged species or radicals would be required but cells should not be exposed to plasma.

3. Acknowledgements

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References


![Fig. 2. The areas of necrosis and gene transfection in 35mm petri dish. (left pair) with grounded metal needle counter electrode. (right pair) with grounded cupper plate counter electrode (The cell and prasmid treatment protcole is described in the references [2][3])](image)
Minimization of contact surface to prevent blood platelet activation

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Thrombosis is a common post-surgery complication after implanting a heart valve or artificial blood vessel of a small diameter. The activation of blood platelets on inner walls of the cardio-vascular implants is particularly pronounced due to rather high blood speed and thus strong shear forces. The platelet activation is minimized by nano-structuring of materials exposed to human blood. Nano-features of lateral dimension well below the diameter of inactivated platelets are formed on the surface of polymeric materials as well as highly oriented graphite upon treatment with non-equilibrium oxygen plasma.

According to the hypothesis the activation of blood platelets on the surface of materials incubated with human blood depends enormously on the contact area between a blood platelet and the surface. Anti-thrombogenic surfaces should have rich morphology in order to minimize the contact area and should be super-hydrophilic in order to assure for right conformation of blood proteins in the thin film formed instantly on the blood facing material upon incubation. Both effects are achieved simultaneously by brief treatment with extremely non-equilibrium oxygen plasma. Figure 1 represents a typical SEM image of untreated highly oriented pyrolytic graphite (HOPG) used as the blood-facing material for heart valves. Large flattened features are well-activated blood platelets.

A SEM image of a plasma-treated HOPG incubated with platelet-rich human blood plasma at same conditions is shown in Figure 2. The surface is nano-rough and super-hydrophilic and only inactivated blood platelets are observed. Similar results are obtained for vascular grafts made from woven polyethylene terephthalate (PET). The untreated material is highly thrombogenic. Figure 3 reveals fibrin fibers making a network on the surface of untreated PET vascular grafts indicating formation of a blood clot. The same material after treatment with oxygen plasma does not allow for such effects as revealed in Figure 4 since only spherical platelets are observed.

Fig. 1. SEM image of untreated HOPG upon incubation with human blood.

Fig. 2. SEM image of untreated HOPG upon incubation with human blood.

Fig. 3. SEM image of untreated vascular graft made from PET polymer upon incubation with human blood.

Fig. 4. SEM image of untreated vascular graft made from PET polymer upon incubation with human blood.
Indium is used for liquid-crystal panels, plasma display panels, and cell phone displays, as well as growth in the application of other technologies that utilized indium-tin oxide (ITO) coatings. Since there were few reports regarding the health effects that arise from exposure to indium compounds, indium was regarded as safe metal. In 2001, a worker engaged as an operator of a wet surface grinder of ITO targets died from bilateral pneumothorax due to interstitial pneumonia [1]. Following the first case was reported in Japan, a potential health risk of occupational exposure to indium particles has been attracted much attention.

We studied the pulmonary toxicity of indium compounds when they were given into the lung of experimental animals. In the study of indium arsenide (InAs) or indium phosphide (InP), those are semiconductor materials, equimolar amounts of indium of those were instilled intratracheally twice a week for 8 weeks [2]. Over a 2-year period, these hamsters were euthanized serially. Weight gain was significantly suppressed in both the InAs and InP groups, compared to the control group, with greater suppression in the InAs group. Histopathologically, severe pulmonary inflammation and localized lesions with bronchiolar-alveolar cell hyperplasia were present in both the InAs and InP groups from just after the last instillation. 

In the study of ITO, we evaluated the chronic pulmonary toxicity of ITO and In2O3, which is the main material of ITO, was also used in order to compare the toxicity of ITO, and it was instilled in equimolar amounts of indium to those of ITO [3]. Hamsters were instilled ITO particles or In2O3 particles, twice a week, for 8 week. The hamsters were euthanized serially up to 78 week. The pulmonary pathological changes in the ITO and the In2O3 groups were almost the same morphologically, and the changes were gradual. Diffuse foci of slight to severe inflammation were present in both the ITO group and In2O3 group during the observation period.

From animal studies, pulmonary toxicity of indium compounds was confirmed when they were instilled into the lung of hamsters. Our results clearly demonstrated that exposure to hardly soluble indium particles represents a risk for interstitial lung damage.

References
Recently, we have clarified plasma fluctuation leads to generation of a large amount of nanoparticles with small sizes using capacitively-coupled reactive discharges with amplitude modulation (AM) [1-4]. In the discharges, behavior of radicals is important because it strongly correlates to nanoparticle growth. Here we obtain information on time evolution of radical generation rates in AM discharges using optical emission spectroscopy to discuss the correlation.

Experiments were carried out using a capacitively-coupled discharge reactor equipped with a two-dimensional laser light scattering (LLS) system [3]. A powered electrode of 60 mm in diameter and 1 mm in thickness was set 20 mm from an upper grounded electrode of 60 mm in diameter. Ar diluted Si(CH\textsubscript{3})\textsubscript{2}(OCH\textsubscript{3})\textsubscript{2} (DM-DOMS) was supplied to the reactor. The flow rate of Ar and DM-DOMS were 40 sccm and 0.2 sccm, respectively. The total gas pressure in reactor was 1.25 Torr. To generate nanoparticles, we sustained a discharge by applying 120 peak-to-peak voltage Vpp of 60MHz to the powered electrode for a discharge period T = 8s. The corresponding discharge power was 30W. For AM discharges, the discharge voltage was modulated with a sinusoidal waveform having a frequency f\textsubscript{AM} = 10, 20, 50, and 100 Hz of the modulation level of 30%. A sheet of laser beam (λ = 532 nm) was passed parallel to the electrodes. Time evolution of the LLS intensity was measured with a high speed camera (FASTCAM SA4: PHOTRON) equipped with an interference filter of a center wavelength of 532 nm at a frame rate of 1000 s\textsuperscript{-1}. To obtain information on time evolution of radical density, we measured Ar emission lines of 750.4 nm and 811.5 nm in Ar diluted Si(CH\textsubscript{3})\textsubscript{2}(OCH\textsubscript{3})\textsubscript{2} discharges by using high speed camera with interference filters of a center wavelength of 750 nm and 810 nm with 10 nm FWHM.

Figure 1(a) shows time evolution of the emission intensities of lines of 750.4 nm and 811.5 nm which are obtained by integrating in the center region of the discharges of 2 × 2 mm\textsuperscript{2} at the same phase of AM. These time behaviors are significantly different from each other. The 750.4 nm emission intensity increases linearly for t = 1 – 4 s, then slightly decreases with time. On the other hand, the 811.5 nm emission intensity slightly increases for t = 1-3 s, then it increases linearly with time. Figure 1(b) shows the time evolution of a ratio R\textsubscript{e} of 811.5nm emission intensity to 750.4 nm one. R\textsubscript{e} represents the Ar metastable density and the density of low energy electrons. Just after the discharge ignition, R\textsubscript{e} decreases for t = 1-2 s. It is almost zero for t = 2-3 s then increases with t. After the discharge ignition, nanoparticles are nucleated and grow in the initial growth phase. These results suggest that the metastable Ar density or low energy electron density increases after buildup the nanoparticles in the discharge region. The spatiotemporal behavior of Ar metastable density is strongly coupled with the nanoparticle growth.

![Graph showing time evolution of Ar I (750.4nm) and Ar I (811.5nm) emissions](image)

Fig. 1. Time evolution of (a) emission intensity of Ar I (750.4nm) and (b) the ratio R\textsubscript{e} of emission from Ar I (811.5nm) and that from Ar I (750.4nm) at the center of the plasma region for AM frequency of 100Hz.

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References
We propose a simple theoretical model that describes correlation between plasma fluctuation and fluctuation of nanoparticle growth in reactive plasmas. The model predicts that the higher density of nanoparticles brings about the smaller mean size, the narrower size dispersion, the sharper size slope at the large size side of the size distribution. The model suggests some methods of tuning the size dispersion and a self-limiting process is the key to suppress remarkably fluctuations in nanostructure fabrication. All of the predictions coincide with the experimental results reported previously. Moreover the model suggests plasma fluctuation induces not only linear response of nanoparticle growth but also nonlinear one.

1. Introduction

Among various kinds of nanotechnology, nanoparticle technology is one of the core nanotechnologies [1-19]. Nanoparticle technology handles the preparation, processing, characterization and applications of nanoparticles, and it makes use of the unique properties of the nanoparticles which are completely different from those of the bulk materials. Nanoparticle technology plays an important role in the implementation of nanotechnology in many engineering and industrial fields including electronic devices, advanced ceramics, new batteries, engineered catalysts, functional paint and ink, drug delivery system, biotechnology, sensors, solar cell, hydrogen storage, etc. One of the important and difficult issues of nanoparticles is to suppress variations of features of nanoparticles, such as their size, size distribution, structure, agglomeration, morphology, surface, defect, dopant, and impurity. Although spatial and temporal fluctuation of nanoparticle fabrication conditions leads to such variations, effects of fluctuations on such variations have not been fully clarified yet.

Up to now, we have studied nanoparticle growth kinetics in low-pressure, high-frequency discharges [1, 7-21]. Based on the results, we have proposed the concept of “plasma nanofactory” which is a miniature version of a macroscopic conventional factory [8]. A plasma nanofactory produces nanoblocks and radicals (adhesives) in reactive plasmas, transports nanoblocks towards a substrate and arranges them on the substrate. We have developed several key control methods for a plasma nanofactory: size and structure control of nanoparticles, control of their agglomeration, transport and sticking, and then have demonstrated the combination of several types of control [8]. Fluctuation control is the key to “plasma nanofactory”.

Here we propose a simple theoretical model that describes correlation between plasma fluctuation and fluctuation of nanoparticle growth in reactive plasmas.

2. Model and results

We consider nanoparticle growth in low pressure reactive plasmas. Initial pristine plasmas consisting of electrons and positive ions turn into dusty plasmas or complex plasmas containing not only electrons and positive ions but also negatively charged nanoparticles, when nanoparticles nucleate and grow there. After nucleation of nanoparticles, there are two growth mechanisms: one is CVD growth, namely, accretion of radicals on nanoparticle surfaces, and the other is agglomeration between nanoparticles. We have clarified the conditions of the transition from CVD growth dominant case to agglomeration dominant one in plasmas [15]. Hereafter we discuss the CVD growth dominant case, because nanoparticles mostly are charged negatively in plasmas and their agglomeration is often suppressed due to coulomb repulsion force between them [15].

We use two rate equations for the analysis: one is the rate equation of density of radicals contributing to the CVD growth of nanoparticles, and the other is the rate equation of nanoparticle growth. For simplicity, we assume one kind of radicals contribute to the CVD growth.

The rate equation of radical density is given by

\[ \frac{dn}{dt} = k_r n_e n_x - D \nabla^2 n - k_s n_x n, \tag{1} \]

where \( n \) is the radical density, \( k_r \) the rate constant of radical generation due to electron impact dissociation of source gas, \( n_e \) the electron density, \( n_x \) the density of source gas, \( D \) the diffusion coefficient of radicals, \( k_s \) the rate constant of reaction between radicals and nanoparticles, \( n_p \) the nanoparticle density. In the right hand side (RHS) of the equation, the first term is the radical generation term, the second one represents diffusive loss rates of radicals to wall, and the third term is the loss rate of radicals on nanoparticles. The wall loss is predominant for tenuous suspension of nanoparticles in plasmas, whereas the loss to nanoparticles becomes more important for dense suspension. The last term of RHS of Eq. (1) is often disregarded, because total surface...
area of nanoparticles is much smaller than the wall area. However we cannot overlook this term if we take into account the characteristic diffusion length to wall and that to nanoparticles.

Since the CVD growth rate of nanoparticles is proportional to the density radicals surrounded to the nanoparticles, the growth rate of nanoparticle diameter is given by

\[ \frac{3d_D}{dt} = C_{it} \]  

(2)

where \( C \) is the proportional constant.

Figure 1 shows the time evolution of size distribution PDF for \( \Gamma = 0 \) (a), and that for \( \Gamma > 1 \) (b). The size distribution keeps its shape with increasing their mean size for \( \Gamma = 0 \). As compared with the size distribution for \( \Gamma = 0 \), the size distribution for \( \Gamma > 1 \) has the three features: the smaller mean size, the narrower size dispersion, and the sharper size slope. Such features are obtained, because growth rate of nanoparticles decreases with increasing their size for \( \Gamma > 1 \). All of the features in Fig. 1 coincide with the experimental results reported previously using amplitude modulation of discharge power [16-20]. The self-limiting growth of nanoparticles brings about these features. A self-limiting process is the key to suppress remarkably fluctuations in nanostructure fabrication, not only for bottom-up processes but also for top-down ones [21].

3. Conclusions

We propose a simple theoretical model that describes effects of correlation between nanoparticles on their growth in reactive plasmas. The following conclusions are obtained in this study.

1) The model predicts that the higher density of nanoparticles brings about the smaller mean size, the narrower size dispersion, the sharper slope at the large size side of the size distribution. All of the predictions coincide with some experimental results reported previously.

2) The model suggests some methods of tuning the size dispersion and a self-limiting process is the key to suppress remarkably fluctuations in nanostructure fabrication.

3) The model suggests plasma fluctuation induces not only linear response of nanoparticle growth but also nonlinear one.

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