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Large-area and low-damage processes for hybrid flexible device fabrications with reactive high-density plasmas driven by multiple low-inductance antenna modules

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Abstract. Plasma generation and control technologies for meters-scale ultra-large-area plasma sources have been developed with multiple low-inductance antenna (LIA) modules, as a promising candidate of ultra-large-area and high-density plasma sources for next-generation processing of hybrid flexible devices. Properties of argon-oxygen mixture plasmas sustained with multiple LIA units have been investigated and surface modifications of polymer substrates using the plasmas have been performed. Ion energy distribution at the sheath edge of the argon-oxygen mixture plasmas showed considerable suppression of ion energies as small as or less than 10 eV. We have examined effect of plasma exposure on surface modification and/or degradation of polymer. Surface analysis of polytetrafluoroethylene (PTFE) exhibited nano-surface modification of the polymer surface without suffering degradation of molecular structures beneath the nano-surface layer.

1. Introduction

Low-damage and nano-surface processes are of key importance for development of next-generation devices including hybrid flexible devices or electronics on polymers. For successful fabrication of devices on polymers, it is significant to develop low-damage plasma sources for fine control of interface between the polymer substrate and inorganic functional films without suffering degradations due to ion bombardment. Furthermore, for enhancement of production efficiency and/or cost reduction in fabrication of these devices, it is significant to develop meters-scale/ultra-large area uniform plasma reactor. In enlargement of source size exceeding a meter, however, plasma distributions hence processing profiles become inherently non-uniform primarily due to non-uniform power deposition profile caused by standing-wave effects.
In order to overcome these constraints, we have developed low-damage plasma technologies with low-inductance antenna (LIA) modules to drive inductively coupled plasmas (ICPs), which can solve the problems in a straightforward manner via low-voltage operation of ICPs to generate high-density and extremely low-damage plasmas for meters-scale ultra-large-area processing [1,2]. Our unique plasma technology is based on principles of multiple operation and integrated control of LIA modules.

In this article, we present issues involved in meters-scale large-area plasma generation and low-damage plasma production with multiple LIA modules. The issues involved in designing of ultra-large area plasma sources are discussed in terms of simulation aided methods based on experimental justifications to demonstrate feasibility of plasma sources exceeding 2 meters for next generation FPD processes. Properties of argon and argon-oxygen mixture plasmas are reported especially for evaluation of ion energy distribution and effects of plasma exposure onto polymer surface will be discussed based on surface analysis of chemical-bonding states via hard x-ray photoelectron spectroscopy (HXPES) at SPring8 (national SOR facility in Japan).

2. Plasma technologies employing multiple low-inductance antenna modules

Major specifications required for the plasma sources to be employed in large-area processes include a) controllability of plasma profile, b) high-density plasma production for raising throughput, c) low plasma potential for high quality processing and d) low-pressure operation for enhanced efficiency of materials-gas consumption and suppression of dust formation. Among them, the specifications b) - d) are mainly dependent on the discharge schemes and/or the plasma excitation frequency, which are to be selected according to requirements in the materials processing. Therefore, many efforts have been focused on the issues to scale up the conventional sources, which meet the process requirements.

However, considering design issues for plasma production with radio-frequency (RF) power sources to scale up the source size exceeding a meter, power deposition profiles and hence process profiles become inherently non-uniform especially due to standing wave effects and/or edge effects, which can not be avoided with increasing source size when the source employs power coupling elements with a scale length equivalent to or as long as the 1/4 wavelength of the RF-power transmission [3-5].

In order to overcome the constraints via active control of power-deposition profile and hence the plasma uniformity, we have developed plasma control technology as illustrated in Fig. 1 [1,2]. The LIA consists of a U-shaped antenna conductor, which is fully covered with dielectric tubing for complete isolation from the plasma [1,2]. With this configuration and integrated control of each module, the RF power supplied to each of the LIA modules can be controlled actively. Our proposal of the unique source configuration and control method can provide breakthroughs to solve the problems with the standing-wave effects.

Figure 1. Schematic illustrations of LIA unit and plasma control system with integrated and independent power control.
3. Simulation-aided designing of meters-scale large-area plasma source

Designs of ultra-large area plasma sources were examined with simulation codes consisting of electromagnetic module, plasma fluid module and electron Monte Carlo module, where argon (Ar) plasmas sustained with 13.56 MHz HF power were simulated. Distributions of plasma density, electron temperature and neutral density were obtained from plasma fluid module, which solved continuity equation and electron energy conservation equation under drift-diffusion approximation.

In the present investigation, the plasma fluid simulations were carried out for a rectangular process chamber with an internal square area of 300 cm and an internal height of 40 cm, as shown in Fig. 2. Ar plasmas at a pressure of 20 mTorr were simulated by installing LIA modules (40-cm width, 16-cm height) on the top plate located at z = 40 cm and plasma profiles were examined at a substrate holder located at z = 0 cm.

Characteristics of plasma density profile sustained with the LIA module were examined by installing two LIA modules, as shown in Fig. 3, in order to evaluate appropriate spacing between LIA modules for obtaining uniform plasmas in multiple antenna configurations. The numerical result plotted in Fig. 3 indicates that proper spacing between LIA modules should be about ~ 50 cm, which is equivalent to FWHM of the profile, for attaining large-area uniformity in the multiple LIA configurations.

Based on the principle mentioned above, a variety of configurations for multiple LIA regime were examined to attain uniform plasma-density profile. One example of designing ultra-large-area source is shown in Fig. 4, in which RF-power inputs to each of LIA modules were set in the range of 500-1200 W. In this example, uniform plasma profile over 200-cm rectangular area was obtained with a non-uniformity of 5.5%.

**Figure 2.** Schematic illustration of process chamber for simulation.

**Figure 3.** Plasma density profile simulated for two LIA modules located at the center of the top plate.

**Figure 4.** Plasma density profile simulated for 300cm x 300cm plasma source.
4. Properties of Ar-O₂ mixture plasmas and low-damage surface modification of polymers

Plasma modifications of polymers have attracted great interests in a variety of fields to utilize polymer materials for advanced engineering applications \cite{6,7} including device fabrications on polymer substrates.

In the plasma processing of polymers, interactions of ions and radicals impinging onto the polymer surface play important roles. For successful treatment of polymers, it is significant to develop low-damage plasma sources in order to control interface between the polymer substrate and functional films without suffering degradations or chemical-structure change of polymers via ion bombardment due to elemental loss and/or bond breaking of polymers. The ion-induced degradation of polymers may cause unwanted change in desired characteristics of polymers as flexible materials; e.g. carburization of polymers due to loss of H, O and N atoms from their chemical chains enhances hardness and brittleness, which in turn lower flexibility in the modified layers and/or adhesion strength of the films formed on them. Thus special attentions should be paid in controlling and/or suppressing the ion damage. Generally, the extent of ion damage in RF plasmas can be evaluated by the ion energies, which are roughly equivalent to potential difference in the sheath between plasma potential and the potential at the substrate surface. As one of the effective plasma sources with suppressed plasma damage, we have developed ICP sources sustained with LIA modules, which allowed a low-voltage operation of ICPs to generate large-area and high-density plasmas \cite{1,2}.

In this section, we report on properties of argon-oxygen mixture plasmas sustained with multiple LIA modules for low-damage processing of polymers. For evaluation of surface-modification characteristics and/or plasma damage during processing of polymers with reactive argon-oxygen mixture plasmas, nondestructive depth-profile analysis of chemical-bonding states has been carried out via hard x-ray photoelectron spectroscopy (HXPES).

4.1. Experimental

Schematic diagram of the chamber installed with a set of 8 LIA units is shown in Fig. 5. The LIA unit consists of a U-shaped antenna conductor, which was fully covered with dielectric tubing for complete isolation from the plasma \cite{1,2}. Eight LIA units with a 70 mm width and a 160 mm height were mounted on the top flange of the discharge chamber and were coupled to a 1000-W RF power generator at 13.56 MHz via a matching network, to which all the LIA units were connected in parallel. The plasma chamber had a 500 mm inner diameter and a 200 mm height, which was connected to a diffusion chamber with a 500 mm inner diameter and a 400 mm height. A water-cooled substrate holder was placed at a distance of 297 mm from the top flange. The base pressure of the chamber evacuated with a turbomolecular pump was 3 x 10⁻⁴ Pa and argon-oxygen plasmas were produced at a total pressure of 2.6 Pa. Here, a partial pressure ratio \( R \) in the argon-oxygen mixture gas is defined as

\[
R = \frac{P_O}{P_{Ar} + P_O},
\]

in which \( P_O \) and \( P_{Ar} \) denote partial pressures of oxygen and argon, respectively.

Kinetic energy distributions of ions impinging onto ground potential from argon-oxygen mixture plasmas were measured using a mass-separated ion-energy analyzer (EQP500, Hiden) mounted on sidewall as shown in Fig. 5. Plasma potential and floating potential were measured with a cylindrical Langmuir probe, which was inserted radially at an axial position of 280 mm below the top flange.

Chemical bonding states in the nano-surface layer of polymers exposed to plasmas were analyzed using HXPES at photon energy of 50 eV; the spectra were obtained after a bombarding ion exposure of 2 x 10¹⁰ ions/cm². The spectra were fitted with a Gaussian line shape using a nonlinear least-square method, and the results were summarized in Table 1.
energy of 7.94 keV. The HXPES measurements were carried out at the national synchrotron radiation facility SPring-8 of the Japan Synchrotron Radiation Research Institute (JASRI). In the chemical analysis of polymer surface with x-ray photoelectron spectroscopy, it is of great significance to employ x-rays in the hard x-ray region because the photoelectrons with hard x-rays have sufficiently longer mean free path (about 20 nm) than that with the conventional characteristic x-ray photons (a few nm). This feature with the HXPES makes it possible to analyze the depth profile of the chemical bonding states via variation of glancing angles for photoelectrons detection from ~90 degrees (surface normal) for analysis of deep regions (~20 nm) down to about 10 degrees for analysis of shallow regions (a few nm) without degradation of the bonding states due to ion milling as in the conventional XPS analysis.

4.2. Results and discussion

First, a typical mass spectrum of the ionic species measured with the mass-separated ion-energy analyzer is shown in Fig. 6 for the argon-oxygen mixture plasma sustained at a partial pressure ratio of 3% \((R = 3\%)\). The mass spectrum shows that the major ionic species in the argon-oxygen mixture plasma are \(\text{Ar}^+\), \(\text{O}_2^+\) and \(\text{O}^+\) ions, indicating that reactivity of the plasma is enhanced via electron-impact ionization, excitation and dissociation of oxygen molecules in the discharge.

Figure 7 shows variations of kinetic energy distribution of atomic oxygen ions \((\text{O}^+)\) measured in the argon-oxygen mixture plasmas sustained at an RF power of 1000 W as a parameter of oxygen partial pressure ratio \(R\). The ion energy distributions observed in the present experiments exhibit considerably suppressed ion energies as small as or less than 10 eV, which is considered to be mainly due to low-voltage operation of ICPs via low inductance antenna units. With decreasing \(R\), the peak ion energy of the energy spectrum is found to decrease slightly from 9.8 eV at \(R = 100\%\) to 8.1 eV at \(R = 3\%). These results suggest that the ICPs proposed in the present investigation are promising for a variety of polymer processes, which require considerable low-damage processing.

Furthermore, potential drop from the plasma potential to the floating potential was evaluated using Langmuir probe measurements. The potential drops measured by subtracting the floating potential from the plasma potential were as low as 6 V, which is slightly smaller than the ion kinetic energy distribution shown in Fig. 7 since the floating potential was measured to be a few volts. Considering that the potential drop is almost equivalent to the energy of ion bombardment during the film growth with plasma CVD on non-conductive substrate such as glass and polymers, the results of ion-energy distribution and potential-drop measurements demonstrate that ICPs sustained with LIA units are attractive as plasma sources for polymer processes, which require low-damage processing with markedly reduced plasma damage by ion bombardment.
As a demonstration for plasma modification of polymers, the argon-oxygen mixture plasma sustained at an oxygen partial pressure ratio $R = 3\%$ was exposed to the surface of polytetrafluoroethylene (PTFE) substrate for 10 min and the surface chemical bonding states were analyzed via HXPEES. Figure 8 shows C1s HXPEES spectra measured for the PTFE sample after exposure to the argon-oxygen mixture plasma with photoelectron detection angle as a parameter. The HXPEES spectra indicate that the CF$_2$ bond (F-C-F) or main chemical bond of the PTFE is maintained from deeper region of about 20 nm to nano-surface layer, while the CO bond increases with decreasing detection angle of photo electrons. The results indicate that nano-surface modification (CO bond formation) of PTFE surface is performed without suffering degradation of major molecular structures of PTFE beneath the surface nano-layer possibly due to low-damage plasma processing with the present plasma source, in which the energy of ion bombardment onto the PTFE surface was measured to be as small as 6 eV.

5. Summary

Plasma generation and control technologies for fabrication of hybrid flexible devices have been developed with multiple low-inductance antenna (LIA) modules. Feasibility of ultra-large-area and uniform plasma sources was demonstrated via numerical prediction with plasma-fluid simulation; indicating that uniform plasma profile over 200-cm rectangular area could be designed with a non-uniformity of 5.5% in the plasma source with 3m x 3m scales to meet requirements in the next-generation processes. Ion energy distributions of atomic oxygen ions in argon-oxygen mixture plasmas showed considerable suppression of ion energies as small as or less than 10 eV. The HXPEES measurements of PTFE surface after exposure to the plasma exhibited nano-surface modification of polymer surface without suffering degradation of molecular structures beneath the nano-surface layer.

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