Development of a loop-type of inductively coupled thermal plasma with molecular gas injection for large-area uniform materials processing

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Abstract: This paper reports a new development of a kW-class loop type of inductively coupled thermal plasmas (loop-ICTP) with molecular gas for large-area materials processing. The loop-ICTP contains a loop quartz tube, a rectangular quartz vessel and two rf induction coils. The 10 kW Ar loop-ICTP with molecular gas could be established almost uniformly over 50 mm just on the substrate with gas temperatures about 4000 K.

Keywords: inductively coupled thermal plasma, large-area processing, uniform thermal plasma

1. Introduction
The inductively coupled thermal plasma (ICTP) has been widely used in various applications such as thermal barrier spray coating [1], nanoparticle synthesis [2], nanotube synthesis [3], transparent conductive oxide deposition [4], diamond film deposition [5], surface modification [6], etc. The ICTP has several advantages of high gas-temperature, high radical density without any contamination. The ICTP is conventionally sustained in a cylindrical tube in electromagnetic field induced by an rf induction coil. However, the conventional cylindrical type of ICTP is hardly suitable to large-area materials processing because it also requires a large volume of the ICTP and more input power. Moreover, it is shrunk by self-pinchoff effect due to Lorentz force.

For the purpose of large-area materials processing, we have already developed a planar type of ICTP (planar-ICTP) [7]. The planar-ICTP uses a rectangular quartz vessel instead of a conventional cylindrical quartz tube, with rf coils located perpendicular to the vessel. We have confirmed that a planar ICTP could be established in the rectangular vessel where the planar ICTP was formed with a ring-like shape. In addition to this, we have newly developed a loop type of ICTP (loop-ICTP), which is composed of a loop narrow quartz tube, a rectangular quartz vessel and two rf induction coils [8]. We successfully established an Ar loop-ICTP in the loop narrow quartz tube stably.

This paper describes experimental results on uniform formation of the novel loop-ICTP on the substrate. The Ar/O2 and Ar/N2 loop-ICTPs as well as Ar loop-ICTP were tested because these molecular gases are widely used in many processing such as oxidation and nitridation etc. A substrate was located downstream of the loop tube outlet, and then the linear thermal plasma is formed just on the substrate. The lateral distributions of radiation intensity from the Ar/O2 and Ar/N2 loop-ICTPs just on the substrate were measured to study the stability and uniformity of the ICTP by a color high speed video camera, and spectroscopic observation. In addition, the vibrational and rotational temperature of N2+ was evaluated along the substrate surface for Ar/N2 loop-ICTP. Finally, we confirmed that Ar/O2 and Ar/N2 loop ICTP could be formed on the substrate stably and uniformly in 60 mm with gas temperature about 3600-3800 K at 10 kW.

2. Principle of loop type of inductively coupled thermal plasmas (loop-ICTP)
Fig. 1 shows a comparison between the conventional cylindrical ICTP and the loop-ICTP developed here. The cylindrical ICTP is sustained in a cylindrical dielectric tube by magnetic coupling. The advantages of the ICTP are to form high gas temperature field without any contamination because of electrodeless discharge. However, this type of ICTP is not easy to be adopted for large-area materials processings. On the other hand, the developed loop-ICTP is formed in a loop narrow tube by magnetic coupling. The thermal plasma is ejected from the two outlets. If the substrate is located under the outlet, ejected thermal plasma lies on the substrate to form a uniform linear thermal plasma there.
Fig. 1. Comparison between a conventional ICTP and a developed loop ICTP.
3. Experimentals for loop ICTP

3.1. Configuration of a loop-ICTP torch

Fig. 2 depicts the actual configuration of the loop-ICTP developed here. It is composed of a loop quartz tube connected to the downstream rectangular quartz vessel. The loop quartz tube has a loop diameter of 100 mm, and an inner tube diameter of 8 mm. At the outlet of the tube, there installed a rectangular quartz vessel with a size of 52.5 mm high and 110 mm wide and 20 mm depth. Inside the rectangular quartz vessel, a Si$_3$N$_4$ substrate is placed with a distance of 6.5 mm from the outlet of the quartz tube. The size of the substrate is 85 mm x 10 mm x 2 mm. Here, a Si$_3$N$_4$ substrate was chosen because it has high melting temperature of 2173 K, thus it is hardly molten and evaporated by ICTP irradiation in a short time. The loop quartz tube is sandwiched by two rf induction coils with the same size to the loop quartz tube. These coils are connected with an inverter rf power source through LC series matching circuit. The coil current supplied from the power source generates magnetic field penetrating the loop tube, and then induced loop electric field along the loop tube. This electric field produces a thermal plasma inside the loop tube.

Fig. 2. Configuration of the developed loop ICTP torch.

3.2. Experimental conditions

The loop-ICTP was sustained by the following condition: Ar gas at a flow rate of 5 slpm, and O$_2$ or N$_2$ at a flow rate of 0.2 slpm were injected from the top port of the tube. Gas pressure inside the chamber was set to 10 and 20 torr. A MOSFET inverter power source with a frequency range of 300 - 400 kHz was adopted for this work. The output power from the power source was fixed at 10 kW. The frequency of the coil current was 356 kHz for Ar/N$_2$ loop-ICTP, and 386 kHz for Ar/O$_2$ loop-ICTP.

The visible light emission from the loop-ICTP was measured with a color high-speed video camera. The frame rate of the camera was set to 1000 frames/s. Spectroscopic observation was also carried out to estimate the radiation intensities of specified atomic lines and the molecular spectra, and the temperature. Fig. 3 indicates the observation positions. They are located at 3 mm above the substrate along the substrate surface. This figure also gives the definition of lateral position $X$ from the center of the substrate surface.

Fig. 3. Spectroscopic observation positions located at 3 mm above the substrate surface.

4. Stable establishment of Ar loop-ICTP

First, experiments were conducted for 100% Ar loop-ICTP to study the stable establishment and its pressure dependence fundamentally. Figs. 4a-d depict visible light emission from Ar loop-ICTP at a frequency of 382 kHz at 10 kW. The Ar gas flow rate is 3 slpm in this case. The Ar loop-ICTP could be established on the substrate stably. At a pressure of 10, 50 and 100 torr, the Ar loop ICTP has high radiation intensity near the outlet of the loop tube. This is due to high gas flow plasma irradiating to the substrate. Increasing pressure improves uniformity of the plasma formed on the substrate. At pressures higher than 200 torr, the Ar loop-ICTP just on the substrate clearly has almost uniform distribution of the radiation intensity.

Fig. 4. Visible light emission from Ar loop-ICTP at 10 kW. Ar gas flow rate is 3 slpm.
5. Ar/O₂ loop type of induction thermal plasmas

5.1. Visible light emission from Ar/O₂ loop-ICTP

Thermal plasmas are well adopted for materials processings with molecular gases. Here, O₂ was added as molecular gas to ICTP. Figs. 5a and 5b present visible light emission from Ar/O₂ loop-ICTP measured by a color high-speed video camera. From a high-speed video camera measurement, the Ar/O₂ loop-ICTP at 10 kW could be established on the substrate very stably at pressures below 20 torr. Increasing pressure above 20 torr made the plasma unstable. At both 10 and 20 torr, the Ar/O₂ loop ICTP has high radiation intensity around the gas inlet. This may be due to thermal pinch by the cooling gas injection of Ar/O₂ there. On the substrate near the outlet of the loop tube, there is a little bit bright region in the ICTP. This also arises from high gas flow plasma irradiating to the substrate. Along the substrate, almost uniform plasma was formed at 20 torr.

Fig. 5. Visible light emission from Ar/O₂ loop-ICTP at 10 kW. Ar/O₂ gas flow rates are 5/0.2 slpm, respectively.

5.2 Spectroscopic observation for Ar/O₂ loop-ICTP and uniformity in radiation intensity

To consider the uniformity of the thermal plasma formed on the substrate, spectroscopic observation was carried out at 3 mm above the substrate. Fig. 6 indicates the emission spectra observed at the center of the substrate. Many Ar atomic lines and O atomic lines could be detected. This means that O atom was produced in the loop plasma on the substrate, and O atom density is important for high-speed oxidation process. Fig. 7 shows the lateral distributions of the radiation intensities from Ar line at 811.5 nm and those from O 777.2 nm at 3 mm above the substrate. The vertical axis is the lateral position X from the center of the substrate. There are strong peaks in the radiation intensity from Ar line near the tube outlet position around X = -40 mm and X = 40 mm at 10 torr. However, it declines at an increased pressure of 20 torr. A similar tendency can be found for the radiation intensity from O line. At 20 torr, we found almost uniform distributions of O intensity, thus excited O atom in 45 mm within a 5% variation.

6. Ar-N₂ loop type of induction thermal plasmas

6.1. Visible light emission from Ar/N₂ loop-ICTP

The Ar-N₂ loop-ICTP could be also sustained on the substrate. Fig. 8 shows the visible light emission from Ar/N₂ loop-ICTP at 10 kW at 356 kHz. Further higher pressure condition extinguishes the Ar/N₂ loop-ICTP. As seen in Fig. 8, for both pressures 10 and 20 torr, there is not locally high intensity point near the tube outlet around X = -40 mm and X = 40 mm, and the plasma on the substrate is almost uniform.

Fig. 6. Emission spectra from Ar/O₂ loop-ICTP at 10 kW observed at the center position X = 0 mm at 3 mm above the substrate.

Fig. 7. Lateral distributions of radiation intensities of Ar I line at 811.5 nm, and O I 777.2 nm from Ar/O₂ loop-ICTP at 10 kW at 3 mm above the substrate.

Fig. 8. Visible light emission from Ar/N₂ loop-ICTP at 10 kW. Ar/N₂ gas flow rates are 5/0.2 slpm, respectively.

6.2. Spectroscopic observation for Ar/N₂ loop-ICTP and uniformity in radiation intensity

Spectroscopic observation was also made to study the state and uniformity of Ar/N₂ ICTP. The emission spectra are plotted in Fig. 9 for Ar/N₂ loop-ICTP at the center X = 0 mm observed at 3 mm above the substrate. As seen, N lines and N₂⁺ 1s*-1s-negative band system were
measured as well as many Ar lines. This indicates that N$_2$ dissociation and ionization occurs markedly in the loop-plasma. On the other hand, 2$^{nd}$ positive band system from N$_2$ was hardly detectable. The above result implies that gas temperature become higher above 3000 K. Fig. 10 depicts the lateral distribution of the radiation intensities from N at 821.9 nm N$_2^+$ at 391.4 nm, and that from Ar at 811.5 nm from the spectroscopic observation. As seen, the radiation intensities are almost constant near the center X ~ 0 mm at both pressures. At a higher pressure 20 torr, the plasma on the substrate is almost uniform with the lateral length of 50 mm in 5% variation for radiation intensities.

![Fig. 9. Emission spectra from Ar/N2 loop-ICTP at 10 kW observed at the center position X=0 mm at 3 mm above the substrate.](image)

![Fig. 10. Lateral distributions of radiation intensities of Ar I line at 811.5 nm, N I line at 821.6 nm and N2+ 1st negative band system at 391.4 nm from Ar/N2 loop-ICTP at 10 kW at 3 mm above the substrate.](image)

6.3. Estimation of vibrational and rotational temperature of N$_2^+$ and their lateral distributions

From spectroscopic observation, the vibrational and rotational temperatures $T_{vib}$N$_2^+$ and $T_{rot}$N$_2^+$ of N$_2^+$ were estimated by fitting theoretically calculated emission coefficient to the measured radiation intensity for 1$^{st}$ negative system. Fig. 11 shows the lateral distribution of estimated $T_{vib}$N$_2^+$ and $T_{rot}$N$_2^+$ at 10 and 20 torr. As seen, the $T_{vib}$N$_2^+$ is almost uniform about 11500 - 12900 K, $T_{rot}$N$_2^+$ is 3100 - 3700 K at 10 torr in lateral region of -40 mm <X< 40 mm. It is also seen that increasing pressure from 10 to 20 torr improves the uniformity in $T_{vib}$N$_2^+$ and $T_{rot}$N$_2^+$. At 20 torr, we have $T_{vib}$N$_2^+$ of 10300 - 11300 K, while $T_{rot}$N$_2^+$ is 3600 - 3700 K in lateral region of -40 mm <X< 40 mm.

![Fig. 11. Lateral distributions of vibrational and rotation temperature of N2+ in Ar/N2 loop-ICTP at 10 kW. These were measured at 3 mm above the substrate.](image)

At pressure condition 10-20 torr, $T_{vib}$N$_2^+$ could be close to electron temperature because there is a large difference of quantum energy levels for vibrational excitation of the order of 0.1 eV. From this reason, Ar/N$_2$ loop-ICTP just on the substrate could have the electron temperature of 11000 - 12000 K. On the other hand, $T_{rot}$N$_2^+$ could be close to gas temperature because of low difference between quantum energy levels for rotation excitation. The above consideration implies that Ar/N$_2$ loop-ICTP just on the substrate has a high gas temperature around 3700 K.

7. Summary

In this paper, experimental results were shown on uniform formation of the novel loop-ICTP on the substrate. The Ar/O$_2$ and Ar/N$_2$ loop-ICTP were treated as a loop-ICTP with molecular gas. As a result, almost a uniform thermal plasma could be established just on the substrate in 50 mm for The Ar/O$_2$ and Ar/N$_2$ loop-ICTP according to spectroscopic observation. The rotational temperature of N$_2^+$ for Ar/N$_2$ loop-ICTP was evaluated to be 3600 - 3800 K along the substrate surface.

8. References