J. Plasma Fusion Res. SERIES, Vol. 8 (2009)

Dynamic behavior of hydrogen and nitrogen radicals in pulse modulated induction thermal plasmas

Tomoyuki ITO, Yasunori TANAKA, Kohei HAYASHI, and Yoshihiko UESUGI

Division of Electrical and Computer Engineering, Kanazawa University

Kakuma, Kanazawa Ishikawa, 920-1192, Japan

(Received: 1 September 2008 / Accepted: 12 January 2009)

Influence of pulse modulation of the coil current sustaining a high-power Ar-N_2-H_2 induction thermal plasma was experimentally studied on the time-averaged particle composition of the thermal plasma. Optical emission spectroscopy measurement was carried out to obtain the time evolution in the relative radiation intensities of excited atoms and molecules flowing into the reaction chamber. The radiation intensities of atomic species like N and H changed faster than those of molecular species N_2^+ and NH. It was also found that, the time-averaged radiation intensities of N and H atomic lines increase by pulse modulation of the coil current, while those of N_2^+ and NH decrease by the pulse modulation under the same time-averaged input power condition. In addition to spectroscopy measurements, the surface temperature of a Ti specimen irradiated by the Ar-N_2-H_2 induction thermal plasma was also measured and was found to decrease by the pulse-modulation. This implies that pulse modulation of the coil current produces more atomic species without increasing heat flux onto the specimen surface.

Keywords: Pulse modulated induction thermal plasmas (PMITP), excited nitrogen atom, excited hydrogen atom, NH molecule, non-equilibrium state, emission spectra.

1. Introduction

Inductively coupled thermal plasmas (ICTPs) have great advantages such as high enthalpy and radical density, and little contamination because of no electrodes. From these advantages, ICTPs are widely used for many material processings like nanopowder synthesis, thin film synthesis, and surface modification etc[1]-[3]. To obtain an effective radical source for high speed surface nitridation process with a temperature control of thermal plasmas, we have developed a pulse modulated induction thermal plasma (PMITP) system[1,4,5]. This PMITP system can modulate the coil current amplitude of the order of several hundreds amperes sustaining an ICTP almost into a rectangular waveform. The pulse-amplitude modulation of the coil current can control the time-averaged temperature in the ICTP. Recently, we also found that the Ar-N_2 PMITP system can produce more excited nitrogen atoms into the reaction chamber with less heat flux compared to the conventional steady state thermal plasmas[4,5]. This feature is useful to high-speed nitridation of metallic surfaces with less thermal damages [4,5]. However, in the actual nitridation processings, hydrogen gas is injected to promote nitridation of the specimen surface [6]. Thus, we investigate effect of the pulse modulation on the behavior of Ar-N_2-H_2 PMITP in this paper.

In the present report, we measured time evolution in the radiation intensities of Ar, N, H, N_2^+ and NH spectra in Ar PMITP with N_2/H_2 additional gases. The radiation intensities are generally proportional to the number density of excited species. The N, H, N_2^+, and NH densities are crucial for rapid surface nitridation process of materials. Furthermore, the time-averaged radiation intensities of these species in modulation plasmas were compared with those in non-modulation plasmas under the same input power to clarify the pulse modulation effect. Time-averaged densities of species are also important because the nitridation process requires several minutes. In addition, the surface temperature of the specimen irradiated by the Ar-N_2-H_2 PMITP was compared to that irradiated by non-modulated plasmas to

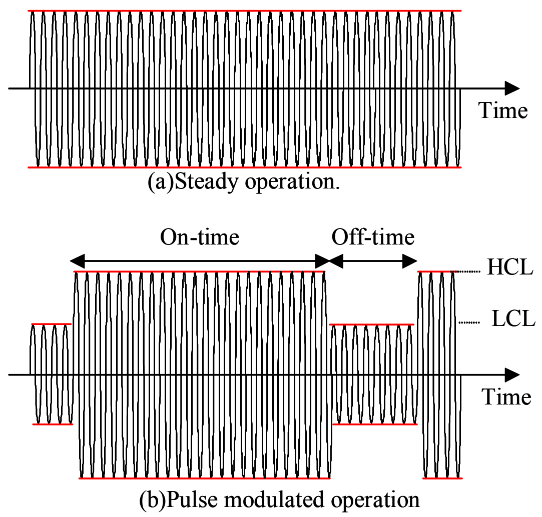


Fig.1. Pulse modulated coil current

author's e-mail:4003itoh@ee.t.kanazawa-u.ac.jp.

obtain the pulse modulation effect on the heat flux onto the specimen surface.

2. Pulse modulation of coil current for PMITP

Fig. 1 shows the schematic diagram of (a) steady state coil current and (b) the pulse amplitude modulated coil current for sustaining a PMITP. The PMITP is established by the amplitude-modulated coil current with a fundamental frequency of 450 kHz in our case. The pulse modulation of coil current induces controllable parameters as indicated in Fig. 1(b). The quantity 'HCL' is the higher current level, 'LCL' is the lower level, 'On time' is the time period with the higher current level and 'Off time' is the time period with the lower current level. We also define 'SCL', shimmer current level as a ratio of LCL/HCL. Setting these four parameters can change dynamic behaviors of the PMITP. The control of these parameters can bring the following expected features and effects: (i) time averaged power and temperature/enthalpy of the thermal plasmas can be controlled in time domain, (ii) extremely high or low electromagnetic field operation can be made during on/off-operation of the coil-current, (iii) thermally and/or chemically non-equilibrium effects in thermal plasma could be introduced by sudden application of the electric field.

3. Experimental setup and conditions

3.1 Experimental arrangements

Fig. 2 illustrates a configuration of the plasma torch for PMITP. The plasma torch is composed of two coaxial quartz tubes with a 330 mm length. The inner tube has an interior diameter of 70 mm. Between these two tubes, cooling water flows to keep the temperature of the tube wall to be 300 K. This plasma torch has an eight-turn induction coil around the quartz tube. Downstream of the plasma torch, a water-cooled reaction chamber is installed. Argon, nitrogen and hydrogen gas mixture was supplied as a sheath gas along the inside wall of the interior quartz tube. A titanium specimen with a diameter of 15 mm and a thickness of 5.0 mm was placed on a water-cooled specimen holder in irradiation experiments. The specimen holder was located at 200 mm below the coil end for specimen surface nitridation. The surface temperature of the titanium specimen was measured using a radiation thermometer. Spectroscopic observation was carried out on the axis of the plasma torch at 200 mm below the coil end from the observation window as depicted in Fig. 2. The light around the observation region is transmitted through a lens, and an optical fiber bundle to the slit of the photo-multichannel analyzer PMA (HAMAMATSU Photonics PMA-12) .This PMA can simultaneously measure spectra in the range 300-900 nm.

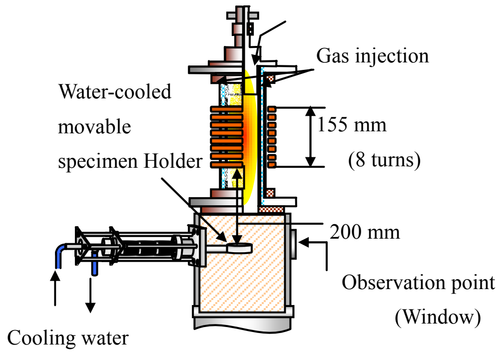
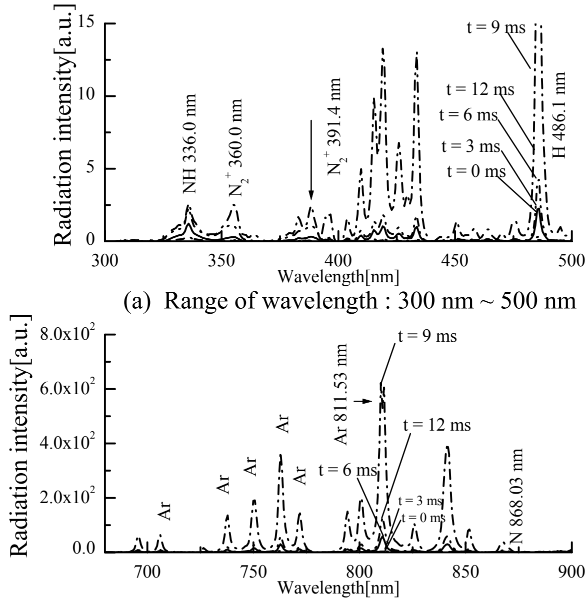


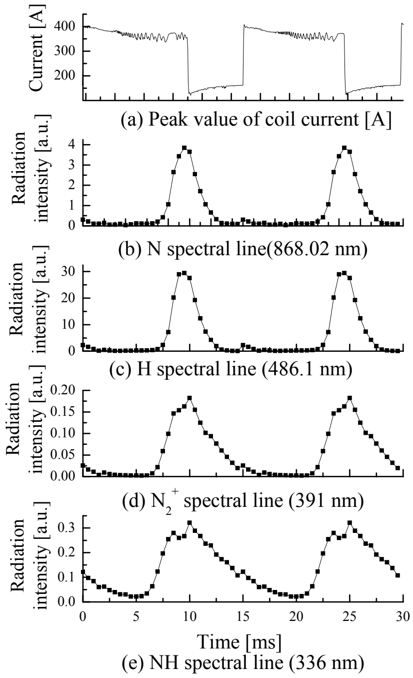
Fig. 2 Schematic diagram of the plasma torch. and the observation position



(a) Range of wavelength : 300 nm ~ 500 nm

(b) Range of wavelength : 500 nm ~ 900 nm

Fig. 3 Emission spectra observed at 200 mm below the coil in Ar-N_2-H_2 PMITP



(a) Peak value of coil current [A]

(b) N spectral line(868.02 nm)

(c) H spectral line (486.1 nm)

(d) N_2^+ spectral line (391 nm)

(e) NH spectral line (336 nm)

Fig. 4 Time evolution in (a) Peak value of coil current, radiation intensity of (b) N, (c) H, (d) N_2^+, and (e)NH spectral line

3.2 Experimental condition

Total gas flow rate was fixed at 100 slpm. Nitrogen and hydrogen gas flow rates were set to 1 and 1 slpm, respectively Pressure inside the chamber was fixed at 230 torr with an automatic feed-back pressure controller. In the present experiment, the on time and off time were fixed respectively at 10 and 5 ms. We also fixed SCL of 40% for any time averaged input power in modulation case. The time-averaged input power was increased by increasing HCL and LCL simultaneously with a fixed SCL. The irradiation time was set to 180 s.

4. Result and discussion

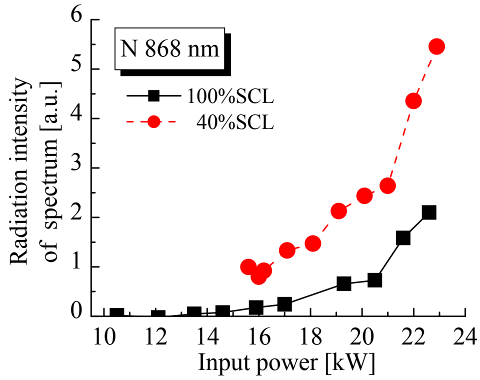
4.1 Time evolution in the radiation intensity of N, H, NH, and N_2^+ spectra

Fig. 3 shows time evolution of the emission spectra observed in the reaction chamber at t=0, 3, 6, 9 and 12 ms, where t is the time from transition from LCL to HCL in the coil current. Here, LCL=160 A and HCL =340 A. As seen, Ar, N and H atomic spectral lines and N_2^+, NH molecular spectra were found to be also modulated with the pulse-modulation of the coil current.

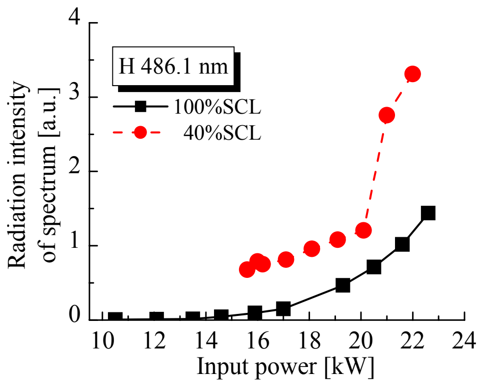
Fig. 4 shows time evolution in (a) the coil-current peak and (b) the radiation intensity of N atomic line at 868.02 nm, (c) that of H atomic line at 486.1 nm, (d) that of N_2^+ molecular spectra at 391.4 nm, and (e) that of NH molecular spectra at 336.0 nm. Here the radiation intensity of the N atomic line at 868.02 nm is in proportion to the number of N(^{4}D°). The radiation intensity of each spectral line was modulated according to the current-amplitude modulation. However, the radiation intensities of molecular spectra such as N_2^+ or NH change more slowly than those of atomic lines such as N or H. Especially, decaying rate of the intensity of N_2^+ and NH spectra is much lower than those of N and H lines. For example, the low decaying rates in the radiation intensity of NH may be due to an increase in NH densities from association processes of N + H + M → NH + M during plasma decaying period, while the number of excited NH decreases with decaying electron temperature.

4.2 Averaged radiation intensity versus input power

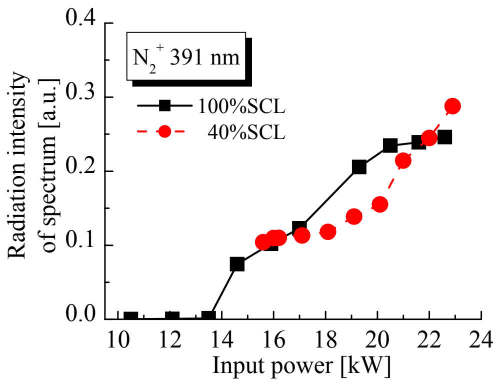
For modification of metal surface, time averaged density of radicals and excited atoms are important as well as instantaneous values of these densities because the surface nitridation requires more than milliseconds. For this reason, time-averaged radiation intensity in modulation condition was estimated, and compared with radiation intensities at 100%SCL. Figs. 5(a), (b), (c) and (d) show the time-averaged radiation intensity of N, H, N_2^+, and NH versus input power for 40%SCL and 100%SCL. As seen in Figs. 5(a) and (b), the radiation



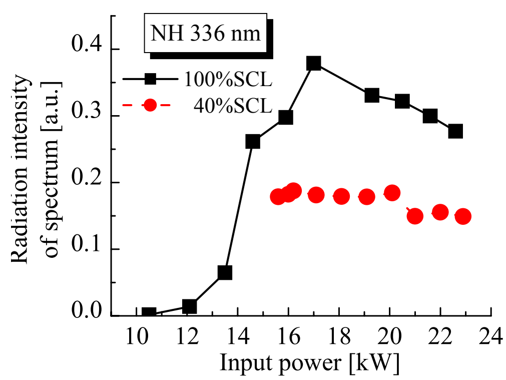
(a) N atomic spectral line



(b) H atomic spectral line



(c) N_2^+ molecular spectral line



(d) NH molecular spectral line

Fig. 5 Dependence of input power of spectral line at 200 mm below of the coil end intensities of atomic species increase with increasing input power generally at 100%SCL. The radiation intensity of N_2^+ also increases with input power and so does the radiation intensity of NH at input power from 10 kW to 17 kW at 100%SCL. However, the radiation intensity of NH decreases with increasing input power from 17 kW to 22 kW. This decrease may be attributable to an increased dissociation rate of NH by the increased electric field strength and increased temperature due to increased input power.

We can also see the effect of the pulse modulation of the coil current on these radiation intensities at the same input power condition from Fig. 5. The radiation intensities of N and H atomic lines increase by the pulse modulation in Figs. 5(a) and (b), which were also seen similarly in our previous work [5]. However, the radiation intensity of N_2^+ is hardly influenced by the pulse modulation. On the other hand, that of NH molecule clearly decreases by the pulse modulation. This decrease in NH intensity arises from more dissociation of NH to produce N and H atoms. However, this more dissociation of NH is not due to higher temperature as described in later section.

4.3. Surface temperature of a titanium

To study the effect of the pulse modulation of the coil current on the heat flux onto the specimen surface, the surface temperature of a titanium specimen located at 200 mm below the coil end was measured using a radiation thermometer for different SCL conditions. Fig.6 depicts the time evolution in the surface temperature of the Ti specimen during and after irradiation of Ar-N_2-H_2 PMITP for 40%SCL, 70% SCL and 100%SCL. The increasing rate of the surface temperature is apparently lower with decreasing SCL. The final surface temperatures at 180 s after irradiation of the PMITP were plotted in Fig. 7 versus input power for 40%SCL, 70%SCL and 100%SCL cases. For any input power condition, the pulse modulation decreases the surface temperature of the specimen. The surface temperature is related directly with the net heat flux following into the surface of the specimen. For this reason, we infer that the net heat flux to the specimen decreases by modulation of the coil current under the same input power condition. Modulation produces a large disturbance in the plasma flow field, and then it effectively might cool the specimen surface by gas flow.

The above results indicate that the pulse modulation can decrease the heat flux onto the surface of the specimen, whereas simultaneously it can increase excited N and H atomic densities onto the surface of the specimen.

5. Conclusions

Influence of pulse modulation of the coil current sustaining a high-power Ar-N_2-H_2 thermal plasma was experimentally investigated on the time-averaged particle composition of the thermal plasma and the surface temperature of a specimen irradiated by the modulated plasma. As a result, we found that the pulse modulation can increase the excited N and H atomic densities and simultaneously decrease the heat flux onto the surface of the specimen. This unique feature could not be obtained by conventional non-modulated plasmas.

[1] T. Ishigaki *et al.*, Sci. Technol. Advanced Master, 6, 111 (2005)

[2] M. Shigeta *et al.*, Thin Solid Film, 457, 192 (2004).

[3] W. R. Chen *et al.*, Surface Coating Technol., **197**, 109 (2005).

[4] Y. Tanaka *et al.*, Appl. Phys. Lett., **89**, 031501, (2006.)

[5] Y. Tanaka *et al.*, IEEE Trans. Plasma Sci., Vol.35, Issue 2, (2007) pp. 197-203.

[6] M. Tamaki *et al.*, Plasmas & lons, **3**, 33 (2000)

[7] Y. Tanaka, 18th Int.Symp. Plasma Chem. ISPC-18, 30P11-23, ID=30, 2007.8, Kyoto, Japan

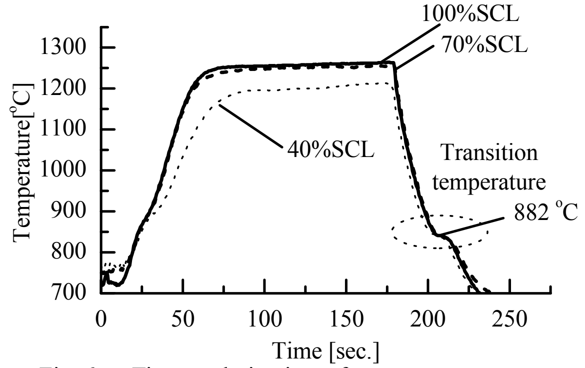


Fig. 6 Time evolution in surface temperature of Ti specimen during and after irradiation of Ar-N_2-H_2 PMITP.

Condition ; Ar 98 slpm, N_2 1 slpm H_2 1slpm, SCL =100%, 70%, 40%

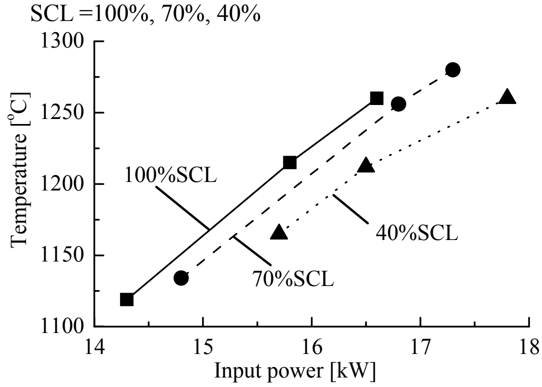


Fig. 7 Dependence of surface temperature of Ti sample on input power.