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Removal of carbon deposited film and hydrogen retention control by low temperature H-C-N reactive plasmas

A.Sasaki[a]*, Y.Takai[a], Y.Uesugi[a], Y.Tanaka[a], T.Ishijima[a], S. Masuzaki[b]

[a]*Kanazawa University, Kanazawa, Ishikawa, Japan*

[b]*NIFS, Toki, Gifu, Japan*

Abstract

Control of tritium retention and its removal from the first wall of future fusion devices are the most crucial issues for safety and effective use of the fuel. Nitrogen injection into edge plasmas has been considered and tested as an effective method for suppression of carbon dust growth and reduction of hydrogen isotope inventory. In this paper we have investigated scavenger effects of nitrogen injected into H_2/CH_4 plasmas using a small helical device where low density (n_e~10^{16} m^{-3}) and low temperature (T_e=5-10 eV) hydrogen plasmas are generated in steady state condition like remote plasmas in fusion devices. It is shown from the comparison of the carbon film deposition and particle growth between those with and without N_2 injection that the chemical erosion effects of nitrogen gas on the carbon film and particle growth strongly depends on the surface temperature. With increasing the surface temperature higher than ~400 K, the nitrogen chemical erosion significantly works to reduce the hydrocarbon deposition.

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PSI-20 keywords: Co-deposition, Dust, Erosion & Deposition, Nitrogen, Sputtering, Surface analysis

**Corresponding author address:* Kakuma, Kanazawa, Ishikawa, Japan.

**Corresponding author E-mail:* me121030@ec.t.kanazawa-u.ac.jp

Presenting author: Aya Sasaki

Presenting author e-mail: me121030@ec.t.kanazawa-u.ac.jp

Body of paper

1. Introduction

Carbon Fiber Composite (CFC) will be used as plasma facing components (PFCs) in ITER hydrogen plasma phase because of their superior thermo-mechanical properties. In the fusion devices using carbon PFCs, carbon materials not only are eroded significantly by hydrogen plasma irradiation but also generate large amounts of dust particles with size of submicron to several tens micron. The hydrocarbon particles generated by chemical sputtering of carbon PFCs containing tritium are transported into scrape off layer (SOL) plasmas and form tritium-containing co-deposits in the cold remote area away from the main interaction area in the divertor plasmas. The control of tritium inventory and suppression of dust particle release is one of key issues for future utilization of carbon materials in the fusion reactor. Nitrogen injection into hydrogen plasmas has been examined as effective methods for suppression of carbon dust growth [1]. In the experiments which are performed with $Ar/H_2/N_2$ plasma irradiation to graphite targets, using high-power inductively coupled plasmas (ICPs), we obtained the results that just a few percent of nitrogen addition (N_2/H_2~2%) into Ar/H_2 plasmas led to significant suppression of agglomeration of carbon particles to form large size carbon dust particles in the number of carbon dust particles [2]. In this experiment it is considered that volatile C-N bond formation may play an important role to restrain cohesion of carbon particles. When compared with other species present in the cold plasma, HCN

shows very high chemical stability (C-N bonding energy is 8.15 eV while N-H is 3.6 eV). In the experiments using ammonia as a carbon-radical scavenger, the deposition rate was drastically suppressed by ammonia injection. It is considered that HCN formation plays an important role to bring suppression effect [3].

In this paper, we have investigated effects of nitrogen addition into H_2/CH_4 mixture plasmas on the formation of carbon film and particles using a small helical device Heliotron-DR, which can generates low density and low temperature, and pure H_2 plasmas in steady state condition. These experimental conditions are useful to study the suppression mechanisms of carbon film formation and tritium retention by nitrogen addition in the remote plasmas of fusion devices rather than ICP.

2. Experimental Setup

Low temperature RF plasmas with H-C-N reactive species were generated in hydrogen plasmas with small amount of CH_4 and N_2 injection. The RF power was about P_{rf} ~2.3 kW using four RF antennas. H_2 gas flow rate was 20 sccm. CH_4 and N_2 gas flow rates were changed between 0.1 to 5 sccm by mass flow controllers. The working gas pressure was 0.3~0.5 Pa. Irradiation time was 10 hours. Figure 1 shows a schematic diagram of the plasma irradiation system. Four RF antennas used for plasma production are located at different toroidal section from the irradiation stages. We use two RF frequencies, 13.56 MHz and 27.12

MHz. The magnetic field of the Heliotron-DR device was generated by toroidal and helical coils. The two helical coils generate the magnetic field with a toroidal pitch number of M=15 and poloidal pole number of l=2. The steady state magnetic fields generated by them were 50 G and 200 G at the plasma center, respectively. The electron temperature and electron density measured by Langmuir probe were 5-10 eV and (0.4-1.6)×10^{16} m^{-3}, respectively at the plasma edge, 15 mm inside from the chamber wall as shown in Fig.1. Four sample holders for plasma irradiation were placed at different toroidal sections. Silicon targets of 10×10 mm^2 were placed on these holders. The samples were electrically floating and the ion energy estimated from the single probe measurements was about 25 eV. The surface temperature of the silicon target could be raised up to ~1,000 K by a ceramic heater which was placed beneath it. A thermocouple was inserted 2 mm below the silicon sample into the BN holder. In this configuration the surface temperature of the sample estimated might be lower a little than the real one. Scanning electron microscope (SEM) was used to observe generated dust particles on the silicon targets. Energy dispersive X-ray spectroscopy (EDS) was also used to examine the components of the dust and deposited layer at an accelerating voltage of 15 kV. To investigate more details like chemical bonding state of the deposited film on the targets, X-ray photoelectron spectroscopy (XPS) was used. Al K_α was used as the incident X-ray and the beam diameter was 400 μm. The thickness of deposited film during irradiation was monitored by a quartz crystal microbalance. The sensor head was placed at ~25 mm inside from the

chamber wall. The silicon targets were placed at 30 mm inside as shown in Fig. 1. An ellipsometer was also used to measure the film thickness on the targets after irradiation. The angles of incidence were 65, 70 and 75°. We assumed that deposited layer consisted of amorphous carbon film and the data were analyzed using a Cauchy relationship. Since the surface coverage of the dust seen by SEM is small, the effect of the dust on the ellipsometry is ignored. Quadrupole mass spectrometer (QMS) and optical emission spectroscopy were used to observe the reactive species in the plasma with H-C-N molecular system.

3. Results and discussion

Figures 2 and 3 show optical emission spectra and mass spectra of H_2/CH_4 plasmas with and without nitrogen addition, respectively. The optical emission spectra were observed along the center of the plasma as shown in Fig. 1. In $H_2/CH_4/N_2$ plasmas, the molecular band spectra of NH and CN radicals were observed strongly compared with H_2/CH_4 plasmas. In this case, gas flow rates of H_2, CH_4 and N_2 were 20, 1 and 1 sccm (N_2/H_2=5%), respectively. When nitrogen gas was added into H_2/CH_4 plasmas, mass spectra measured at the pumping manifold show drastic increases of volatile nitrogen particles like CN, HCN and NH_3 compared to those without nitrogen. For example, the mass of 26 contains both CN and C_2H_2. However the increase of ion current intensity of mass 26 was markedly observed when nitrogen was introduced, so the particles containing CN bond was expected to be dominant in

the present experiment. C≡N bonding energy is higher than those of usually formed in C-H-N low temperature plasmas, such as C-H, C=C, C≡C (C-H:435 kJ/mol, C=C:602 kJ/mol, C≡C:838 kJ/mol, C≡N:887 kJ/mol). Formation of stable molecules like HCN, C_2N_2 can interfere with carbon agglomeration and film formation on the wall. In addition it should be noted that the formation of volatile HCN and NH_3 molecules also has a possibility of suppression of hydrogen retention in the wall.

After H_2/CH_4 and $H_2/CH_4/N_2$ plasmas irradiation, dust particles formed on the silicon targets were observed by SEM. From EDS analysis, it was found that the dust particles were mainly composed of hydrogenated amorphous carbon regardless of the nitrogen injection rate. Figure 4 shows particle size distribution, which was observed on the silicon targets after H_2/CH_4 plasmas irradiation with and without N_2 addition. The surface temperature T_s of the target during plasma exposure was kept at T_s ~430 K. Most of observed particles were smaller than ~2.0 μm. The density of dust particles decreased from ~350 to ~100 mm^{-2} after $H_2/CH_4/N_2$ plasmas irradiation compared to that without nitrogen addition. The average particle diameter was 1.8 μm and 2.0 μm after plasma irradiation with and without nitrogen addition, respectively. Both generation and growth of particles were interfered by nitrogen addition.

Figures 5(a) and (b) show the film thickness and the average diameter of dust particles as a function of T_s. After H_2/CH_4 plasma irradiation, the thickness of carbon film gently increases

with T_s. On the other hand, the film thickness of the targets exposed by $H_2/CH_4/N_2$ plasmas strongly depends on the surface temperature. Although the thickness of carbon film increased by nitrogen injection in relatively low surface temperature (T_s~320 K), it is drastically decreased by nitrogen addition when the surface temperature was higher than ~400 K. From Fig. 5(b), it is found that the effect of the nitrogen addition on the carbon particle agglomeration is relatively weaker than that on the film formation.

Figure 6 shows carbon film thickness as a function of added N_2 ratio to H_2 and CH_4. The gas flow rate of CH_4 was fixed at 1 sccm. The ratio of N_2/CH_4 was changed between 0 and 100%. When the ratio of N_2 to H_2 was 5%, the growth of carbon film strongly depended on the surface temperature. On the other hand, in the case that N_2/H_2 was less than 5%, the film thickness was reduced compared to one without nitrogen injection regardless of its surface temperature. According to the literatures [4, 5], the dependence of the carbon film growth rate on the amount of nitrogen and the surface temperature cannot be explained by a simple physical sputtering mechanism. The rise of the surface temperature is expected to increase surface chemical reactions, i.e. the surface reaction, which in turn, plays a main role in the desorption of surface bound CN species and the formation of the deposited carbon films [4-7].

C1s narrow spectrum of the sample observed by XPS measurement is shown in Fig. 7. The sample was exposed to $H_2/CH_4/N_2$ plasmas keeping its surface temperature low at T_s=320 K. The flow ratio of nitrogen gas to hydrogen was 5%. In that case the film deposition is

promoted by nitrogen injection. N1s peak was also clearly observed on the target surfaces after $H_2/CH_4/N_2$ plasmas irradiation. The C1s spectrum shown in Fig. 7 can be decomposed into two peaks. The binding energy values for the different C1s contributions are 284.4 eV and 285.5 eV. The low C1s binding energy of 284.4 eV is assigned to C-C bond and that of 285.5 eV to C-N bond. From XPS measurements, it is found that the deposited film formed by $H_2/CH_4/N_2$ plasmas contain C-C and C-N bond. These results given by XPS analysis indicate that nitrogen addition brings the growth of the carbon film with nitride carbon in the case that the surface temperature of the target is relatively low (T_s~320 K), which might leads the enhancement of the carbon film growth. When T_s is higher than ~400 K, although C-N bond is formed in the carbon particle and film on the target surface, chemical reactions to form volatile HCN molecules dominate over those of carbon agglomeration. Consequently, carbon film formation is strongly suppressed at the elevated T_s.

The chemical erosion of deposited carbon films by added nitrogen, where formation of C-N bonding has an important role, is also our concern. To investigate nitrogen contribution to the chemical erosion of deposited carbon films, we evaluated the carbon film thickness on the Si target surface after H_2 plasmas or H_2/N_2 mixture plasma irradiation. The carbon film was deposited for 10 hours by H_2/CH_4 plasma irradiation in advance. The gas flow rates of H_2 and N_2 were 20 sccm and 1 sccm, respectively. In the case of T_s~550 K, the film thicknesses were reduced to 16 nm and 11 nm from 48 nm by H_2 and H_2/N_2 plasmas irradiation,

respectively. Reductions of carbon film thickness were also observed when T_s~320 K and ~500 K when nitrogen gas was added to hydrogen plasmas. From the results of film thickness measurement, it is considered that the chemical erosion of the deposited hydrogenated carbon film is enhanced by nitrogen addition to hydrogen plasmas. From these experimental results, both scavenger effects of added nitrogen that the precursor reactive particles, C_xH_y are reduced in the gas phase and chemical erosion by reactive nitrogen radicals on the sample surface are occurred. Further experimental studies are necessary to conclude which process, surface or gas phase reactions, is the key mechanism in the present experiments.

4. Conclusions

The effects of nitrogen addition on the carbon film deposition in H_2/CH_4 low temperature plasmas were studied using low temperature RF plasmas with H-C-N reactive species in Heliotron-DR. The deposition of hydrogenated carbon films strongly depends on the surface temperature of the Si samples and the amount of N_2 addition. When the surface temperature is higher than ~400 K, the carbon film deposition and dust particle growth are dramatically suppressed by nitrogen addition. On the other hand, when the surface temperature is low (~320 K) and the additive rate of N_2 to H_2 is 5%, the carbon deposition is strongly promoted by nitrogen addition. When the additive rate of N_2 to H_2 is less than 3.5%, however, the carbon film deposition is strongly suppressed in the wide surface temperature range from

~320 K to ~600 K. It is found from XPS measurements that the carbon film exposed by $H_2/CH_4/N_2$ plasmas contains C-N bond in the film. The volatile molecules like CN and HCN were observed from $H_2/CH_4/N_2$ plasmas by spectroscopy. The generation of CN radicals in the gas phase and on the carbon film surface would have important role for suppression of hydrogenated carbon film growth. However, it is not clear so far which processes, surface chemical erosion by nitrogen radicals or scavenger effects of nitrogen in the gas phase reaction, is the dominant process for reduction of carbon film deposition. The gas phase reaction of nitrogen with H and C may lead to exhaust of carbonized molecules from the volume, since the formation of volatile CN and HCN molecules stops carbon agglomeration in the gas phase and on the material surface. In addition HCN formation on the carbon film surface may also contribute to reduce the hydrogen retention in the deposited hydrogenated carbon film.

Acknowledgement

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Figure captions

Fig. 1. Schematic diagram of plasma irradiation system in Heliotron-DR.

Fig. 2. Optical emission spectra from H_2/CH_4 (bottom) and $H_2/CH_4/N_2$ (top) plasmas. The observation point is shown in Fig. 1.

Fig. 3. Mass spectra of H_2/CH_4 and $H_2/CH_4/N_2$ plasmas. The expected molecules from the mass spectra are shown in the figure. The gas flow rate of H_2, CH_4, and N_2 were 20, 1 and 1 sccm, respectively.

Fig. 4. The particle size distribution of the two case that irradiated by H_2/CH_4 or $H_2/CH_4/N_2$ plasmas. The gas flow rate of H_2, CH_4, and N_2 were 20, 1 and 1 sccm, respectively. Surface

temperature T_s is shown in the figure.

Fig. 5. Surface temperature dependence of film thickness (a) and diameter of single carbon dust particles (b) observed on the target exposed to H_2/CH_4 and $H_2/CH_4/N_2$ plasmas for 10 hours. The gas flow rate of H_2, CH_4, and N_2 were 20, 1 and 1 sccm, respectively. The broken line and the solid line in the figure show the experimental data of each of without and with nitrogen.

Fig. 6. Carbon film thickness triangles and CN radiation intensity circles as a function of the nitrogen additive rate N_2/H_2. The film thickness data were taken in the two case of surface temperature ~320 K and ~400 K.

Fig. 7. C1s spectrum of carbon film on the target exposed to $H_2/CH_4/N_2$ plasmas. The experimental data was decomposed to two peaks by the Voigt fitting curve. The gas flow rate of H_2, CH_4, and N_2 were 20, 1 and 1 sccm, respectively.

Figures

Fig. 1.

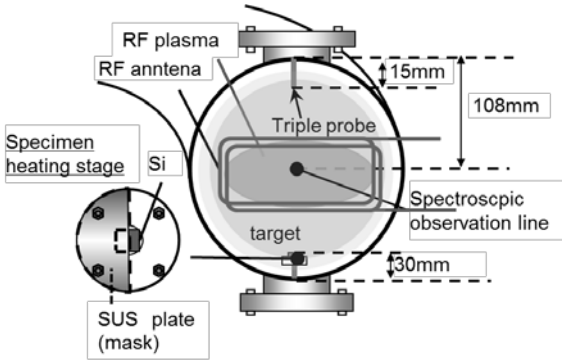


Fig. 2.

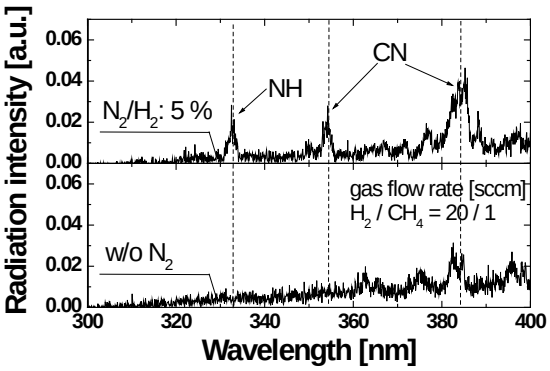

Radiation intensity [a.u.]
0.06
0.04
0.02
0.00
N2/H2: 5 %
NH
CN
gas flow rate [sccm]
H2 / CH4 = 20 / 1
w/o N2
300
320
340
360
380
400
Wavelength [nm]

Fig. 3.

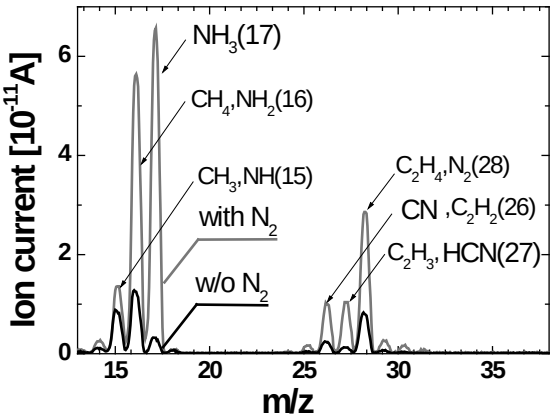

NH3(17)
CH4,NH2(16)
CH3,NH(15)
with N2
w/o N2
C2H4,N2(28)
CN ,C2H2(26)
C2H3,HCN(27)
Ion current [10-11A]
m/z
0
2
4
6
15
20
25
30
35

Fig. 4.

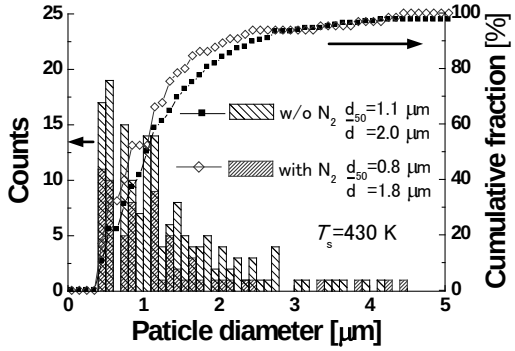

Counts
Cumulative fraction [%]
Paticle diameter [μm]
w/o N2 d50=1.1 μm
d =2.0 μm
with N2 d50=0.8 μm
d =1.8 μm
Ts=430 K
0
5
10
15
20
25
0
20
40
60
80
100
0
1
2
3
4
5

Fig. 5.

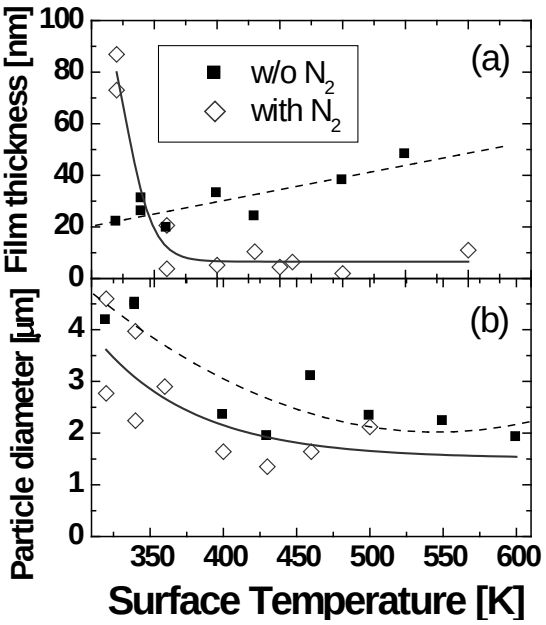

Film thickness [nm]
Particle diameter [μm]
Surface Temperature [K]
w/o N2
with N2
(a)
(b)
100
80
60
40
20
0
4
3
2
1
0
350
400
450
500
550
600

Fig. 6.

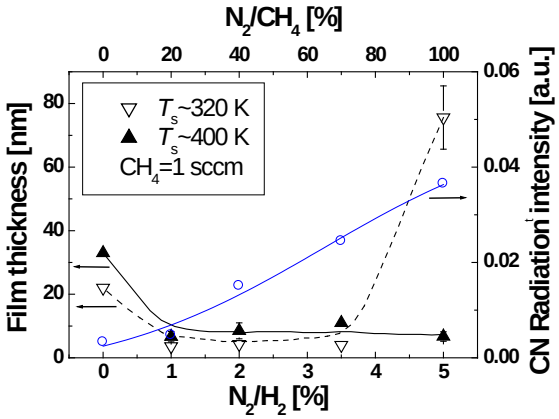
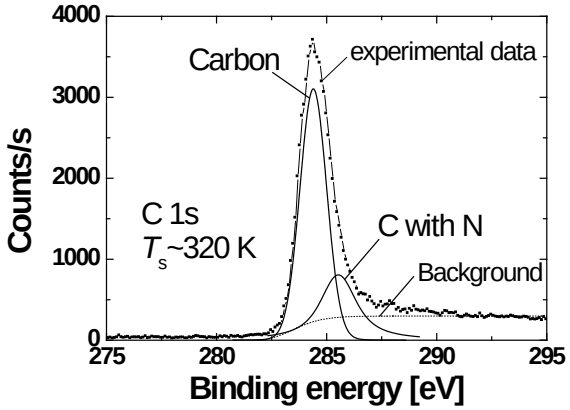

N2/CH4 [%]
0
20
40
60
80
100
Ts~320 K
Ts~400 K
CH4=1 sccm
Film thickness [nm]
CN Radiation intensity [a.u.]
0.06
0.04
0.02
0.00
N2/H2 [%]
1
2
3
4
5

Fig. 7.


4000
3000
2000
1000
0
Counts/s
275
280
285
290
295
Binding energy [eV]
Carbon
experimental data
C 1s
T_s~320 K
C with N
Background