CHIN. PHYS. LETT. Vol. 26, No. 5 (2009) 055202

The influence of Exciting Frequency on N_2 and N_2^+ Vibrational Temperature of Nitrogen Capacitively Coupled Plasma *

HUANG Xiao-Jiang(黄晓江), XIN Yu(辛煜)**, ZHANG Jie(张杰), NING Zhao-Yuan(宁兆元)***

Jiangsu Key Laboratory of Thin Films, School of Physical Science and Technology, Soochow University, Suzhou 215006

(Received 11 December 2008)

By using optical emission spectroscopy (OES), N_2 and N_2^+ vibrational temperatures in capacitively coupled plasma discharges with different exciting frequencies are investigated. The vibrational temperatures are acquired by comparing the measured and calculated spectra of selected transitions with a least-square procedure. It is found that N_2 and N_2^+ vibrational temperatures almost increase linearly with increasing exciting frequency up to 23 MHz, then increase slowly or even decrease. The pressure corresponding to the maximum point of N_2 vibrational temperature decreases with the increasing exciting frequency. These experimental phenomena are attributed to the increasing electron density, whereas the electron temperature decreases with exciting frequency rising.

PACS: 52.25.−b, 52.70.Kz, 52.80.Yr

Capacitively coupled plasma (CCP) has been widely used in the ultra-large scale integrated (ULSI) circuit process for deposition, etching and surface treatments.[1] As the device dimension is continuously shrinking in ULSI chips, the traditional capacitive reactor equipped with the conventional radio-frequency 13.56 MHz source has been unable to meet current demands for the independent control of ion flux and ion bombardment energy on the substrate. In order to realize this goal, very high frequency (VHF) sources such as 27 MHz, 41 MHz or even higher and rather low frequency sources (2 MHz, 700 KHz, etc) are used, respectively.[2−8] Due to the promising features of the so-called dual-frequency (DF) CCP in plasma characteristics suitable for the microelectronic industry, more attention has been paid by now to the electron heating mechanism, bulk plasma and plasma sheath properties using numerical and analytical methods. In addition, various plasma diagnostics have also been applied into plasma measurements and diagnosis in the past years.

Apart from the full understanding of distribution of electron and ion and even active radicals in the plasma, another important parameter, neutral gas temperature during plasma treatment, should also be focused on since the neutral particle density changes as a result of the neutral gas temperature changes for constant pressure processes, which in turn can cause the neutral to ion flux ratio and hence the etching rate and profile to change. Because of the importance in different areas of industrial plasma applications, the rotational and vibrational temperatures of N_2 and N_2^+ have been more extensively studied in recent years.[9−20] It should be noted that in non-equilibrium plasmas, these temperatures are not only different from the gas kinetic temperature but also from each other.[16,17] In certain cases, the rotational temperature is roughly equal to the gas temperature, which can be regarded as an indicator of the gas temperature in non-equilibrium plasmas.[9−14] However, a vibrational temperature is indicative of chemically reactive of a vibrational excited specie, and provides insight about the relative rates of vibration-vibration and vibration-translation energy exchange processes.[17] Nassar *et al.*[18] used the first negative and second positive overlapped molecular systems to determine the rotational and vibrational temperatures and the ratio of N_2^+/N_2 by using OES. Rehman *et al.*[19] calculated the vibrational temperature of second positive and first negative system of N_2, and discussed the effect of neon mixing in nitrogen plasma. Sakamoto *et al.*[20] studied the vibrational populations of N_2 $C^3\prod$ and $B^3\prod$ states in a microwave discharge by spectroscopic technique . We have investigated the influence of exciting frequency on N_2 and N_2^+ rotational temperatures in nitrogen capacitively coupled plasma and found the effective ion heating and/or possible resonant heating in the bulk under the low-frequency field.[15] However, few researches on influence of the frequencies on N_2 and N_2^+ vibrational temperatures in CCP plasma have been reported.

In this Letter, the N_2 and N_2^+ vibrational temperatures in CCP discharges with different rf frequencies from 2 MHz to 41 MHz are deduced by measuring bands of N_2 emission spectra. The method of comparing the measured and calculated spectra of selected transitions with a least-square procedure [11,15,21] is used in our study. The changes of the N_2 and N_2^+ vibrational temperatures with the effect of the rf exciting frequency and plasma parameters are discussed.

*Supported by the National Natural Science Foundation of China under Grant Nos 10635010 and 10775103.

**Email: xylzf_1999@suda.edu.cn

***Email: zyning@suda.edu.cn

© 2009 Chinese Physical Society and IOP Publishing Ltd

In the experiment, the CCP reactor is 350 mm in inner diameter, and consists of two flat electrodes with the upper electrode diameter of 220 mm and the lower of 200 mm. The upper water-cooled electrode is the powered one, driven by a power amplifier connected with a signal generator with its frequency changing from 2 MHz to 41 MHz, and the network is an L-typed configuration composed by two variable capacitors and a variable inductor. The lower electrode is connected to the ground in this experiment. The gap between two flat electrodes is fixed at 30 mm. Pure N_2 (99.995%) is introduced via a mass flow controller into the chamber. An OES (Avaspec-2048FT-8RM) equipped with a CCD detector is used to monitor the optical emission along the midplane from the N_2 CCP discharges with its spectral resolution of 0.05–0.13 nm, and the range of wavelength from 200 nm to 900 nm. N_2 spectra are typically acquired from 300 nm to 500 nm, which contains most of the N_2 second positive system $\left(C^3\prod_u - B^3\prod_g\right)$ and from the N_2^+ first negative system $\left(B^2\sum_u^+ - X^2\sum_g^+\right)$.

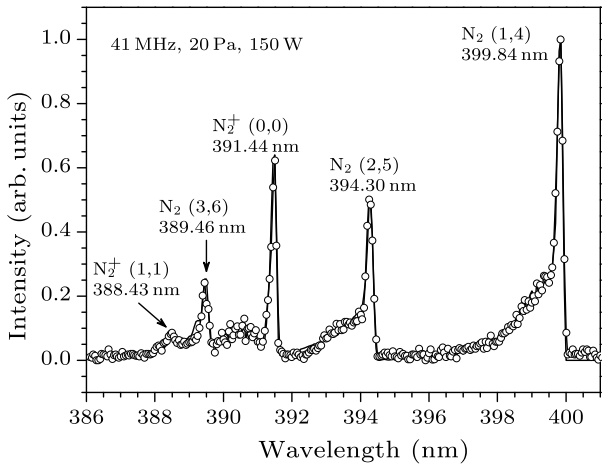


Fig. 1. Measured and calculated nitrogen optical emission spectroscopy for a 20 Pa discharge sustained with 41 MHz 150 W.

Although the excited states of N_2 and N_2^+ can be formed by electron excitation from the ground state or collision with the metastable state, the electron excitation from the ground state is the main process. The electron is too light to cause a significant change in the moment of N_2 and N_2^+. Therefore, as in past works,[10,18,22] we assumed that the excited states of N_2 and N_2^+ are mainly caused by electron excitation from ground state, and the vibrational temperature of the excited state is equal to that of the ground state. It is also assumed that the emitting N_2 or N_2^+ can be described by a Maxwell–Boltzmann distribution characterized by a single rotational and vibrational temperature. We choose the N_2^+ first negative system $(B^2\sum_u^+ - X^2\sum_g^+)$ and N_2 second positive system $(C^3\prod_u - B^3\prod_g)$ overlapped molecular emission optical spectrum, which covers from 386 nm to 400 nm in the N_2 optical emission spectrum to measure the N_2 and N_2^+ vibrational temperatures. The details of the method of measuring the N_2 and N_2^+ vibrational temperatures are described elsewhere.[21]

Figure 1 shows the fitting result of the measured line at the condition of 150 W for 41 MHz rf input power and 20 Pa for discharge pressure. The simulated line corresponds to N_2 vibrational temperature of 3052 K, and N_2^+ vibrational temperature of 1707 K, which is very close to the measured line with the squared difference between calculated and measured normalized intensities $\delta = 0.07$.

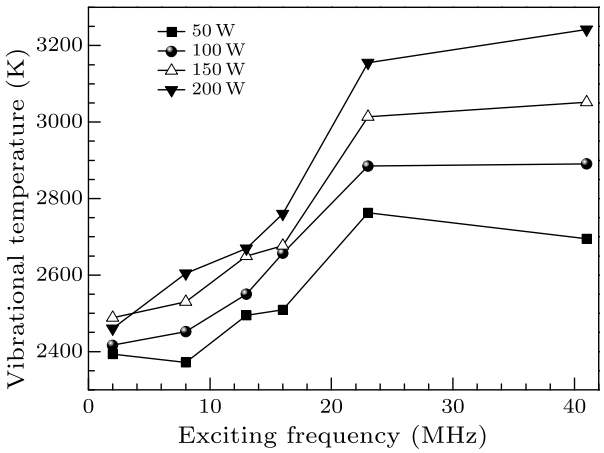


Fig. 2. Vibrational temperature of N_2 versus exciting frequency for different input rf powers at pressure 20 Pa.

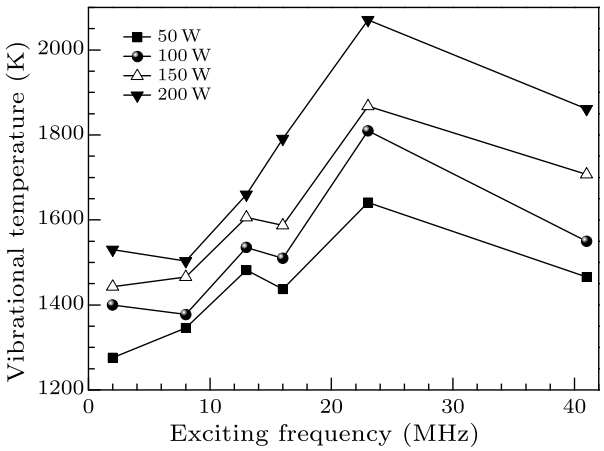


Fig. 3. Vibrational temperature of N_2^+ versus exciting frequencies for different input rf powers at pressure 20 Pa.

The N_2 and N_2^+ vibrational temperatures in the capacitively coupled plasma are measured as functions of exciting frequency and rf input power as shown in Figs. 2 and 3, with the corresponding discharge pressure fixed at 20 Pa. The N_2 and N_2^+ vibrational temperatures show large differences, in which the N_2 vibrational temperature is much higher than that of N_2^+. The reason for this is that the decay rate of the vibrational distributions is much faster than the vibrational

energy transfer rate and energy exchange between the vibrational distributions can be neglected due to effectively decoupling for the two distributions. Viewed from Fig. 2, the N_2 vibrational temperature almost increases linearly with increasing exciting frequency up to 23 MHz. With further increase of the exciting frequency, the temperature seems to be saturated for the different rf input power, but a slight drop for the lower rf input power. The N_2^+ vibrational temperature also increases firstly with increasing exciting frequency and then decreases gradually after experiencing a temperature maximum around 23 MHz under different rf input powers as shown in Fig. 3.

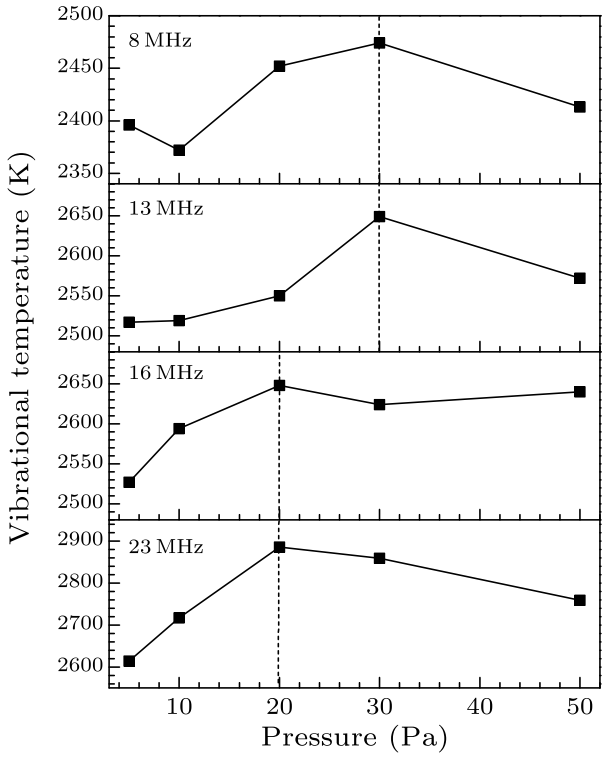


Fig. 4. Vibrational temperature of N_2 versus pressure for different exciting frequencies at input rf power 100 W.

It is known that the vibrational temperature is related to vibrational excited particle density n_v, the increase of vibrational temperature indicates an increase in relative population of vibrational excited particles. The relative population of the vibrational excitation particles is related to both electron density n_e and the electron temperature T_e in the plasma.[23] The density of electron increases sharply with the exciting frequency increasing at a fixed input power.[24] Thus n_e increases with exciting frequency and leads the N_2 vibrational temperature to increase linearly with the increasing exciting frequency firstly. However, the increase of n_e makes the electron collision frequency rise and leads T_e to decrease in the plasma bulk.[25] Therefore, the N_2 vibrational temperature may become of T_e-dominated influence on the vibrational exciting rather than n_e-dominated with exciting frequency further increasing. This results in the fact that the increment of N_2 vibrational temperature becomes slower at high power, and even appears decreasing at low power. For the same reason, the N_2^+ vibrational temperature also increases firstly with exciting frequency increasing and then appears to decrease much in evidence for each power.

Figure 4 shows N_2 vibrational temperature versus pressure for the different exciting frequencies at 100 W. The maximum of N_2 vibrational temperature appears at about 30 Pa for 8 MHz and 13 MHz at 100 W. However, the maximum point of N_2 vibrational temperature shifts to the point at about 20 Pa for the same input power and the exciting frequencies of 16 MHz and 23 MHz. This indicates that the pressure for the maximum of N_2 vibrational temperature decreases with exciting frequency increasing. As described above, the higher exciting frequency has higher n_e and lower T_e. The increment of pressure, which increases the particle collision frequency, can also cool the electron temperature. Hence, the higher the exciting frequency or the pressure, the lower the value of T_e. Therefore, the changing point for n_e-dominated to T_e-dominated influence on vibrational exciting corresponds to the higher pressure at lower exciting frequency, while it corresponds to the lower pressure at higher exciting frequency. This leads the pressure for maximum point of N_2 vibrational temperature to decrease with exciting frequency increasing.

In conclusion, we have studied the influence of exciting frequency from 2 MHz to 41 MHz on N_2 and N_2^+ vibrational temperatures of nitrogen capacitively coupled plasma by OES. It is found that N_2 and N_2^+ vibrational temperatures almost increase linearly with increasing exciting frequency up to 23 MHz. After that, the increment of N_2 vibrational temperature becomes slower at high power and even appears to decrease at low power, while the N_2^+ vibrational temperature appears to decrease much in evidence for each power. The pressure corresponding to the maximum point of N_2 vibrational temperature decreases with exciting frequency increasing. These are all due to the electron density increasing whereas the electron temperature decreases with exciting frequency rising.

References

[1] Lieberman M A and Lichtenberg A J 2005 *Principles of Plasma Discharges and Materials Processing* (New York: Wiley) p 14
[2] Lee C, Hiromitsu K, Masaaki H and Akira K 2005 *Solid State Technol.* **11** 39
[3] Lee J K, Manuilenko O V, Babaeva N Y, Kim H C and Shon J W 2005 *Plasma Sources Sci. Technol.* **14** 89
[4] Kim H C, Lee J K and Shon J W 2003 *Phys. Plasmas* **10** 4545
[5] Jiang W, Xu X, Dai Z L and Wang Y N 2008 *Phys. Plasmas* **15** 033502
[6] Li X S, Bi Z H, Chang D L, Li Z C, Wang S, Xu X, Xu Y,

Lu W Q, Zhu A M and Wang Y N 2008 *Appl. Phys. Lett.* **93** 031504
[7] Yuan Q H, Ye C, Xin Y, Huang X J, Ning Z Y and Yin G Q 2008 *Appl. Phys. Lett.* **93** 071503
[8] Xu Y J, Ye C, Huang X J, Yuan J, Xing Z Y and Ning Z Y 2008 *Chin. Phys. Lett.* **25** 2942
[9] Shota N, Michio K and Hiroshi A 2006 *Plasma Sources Sci. Technol.* **15** 783
[10] Bai B, Sawin H H and Cruden B A 2006 *J. Appl. Phys.* **99** 013308
[11] Tuszewski M 2006 *J. Appl. Phys.* **100** 053301
[12] Cruden B A, Rao M V V S, Sharma S P and Meyyappan M 2002 *J. Appl. Phys.* **91** 8955
[13] Donnelly V M and Malyshev M V 2000 *Appl. Phys. Lett.* **77** 2467
[14] Hash D B, Bose D, Rao M V V S, Cruden B A, Meyyappan M and Sharma S P 2001 *J. Appl. Phys.* **90** 2148
[15] Huang X J, Xin Y, Yuan Q H and Ning Z Y 2008 *Phys. Plasmas* **15** 073501
[16] Koike S, Sakamoto T, Kobori H, Matsuura H and Akatsuka H 2004 *Jpn. J. Appl. Phys.* **43** 5550
[17] Biloiu C, Sun X, Harvey Z and Scime E 2006 *Rev. Sci. Instrm.* **77** 10F117
[18] Nassar H, Pellerin S, Musiol K, Martinie O, Pellerin N and Cormier J M, 2004 *J. Phys. D: Appl. Phys.* **37** 1904
[19] Rehman N U, Khan F U, Khattak N A D and Zakaullah M 2008 *Phys. Lett.* A **372**, 1462
[20] Sakamoto T, Matsuura H and Akatsuka H 2007 *J. Appl. Phys.* **101** 023307
[21] Huang X J , Xin Y, Yang L , Yuan Q H and Ning Z Y 2008 *Phys. Plasmas* **15** 113504
[22] Mi L, Xu P and Wang P N 2005 *J. Phys.D: Appl. Phys.* **38** 3885
[23] Kang Z D and Pu Y K 2002 *Chin. Phys. Lett.* **19** 211
[24] Zhu X M, Chen W C, Zhang S, Guo Z G, Hu D W and Pu Y K 2007 *J. Phys. D: Appl. Phys.* **40** 7019
[25] Abdel-Fattah E and Sugai H 2003 *Appl. Phys. Lett.* **83** 1533