20PB-079

Observation of free radicals in the microwave discharge flow of C_6H_6/N_2 gas mixture

C_6H_6/N_2混合気体のマイクロ波放電フローにおけるラジカル計測

Akira Kojima, Haruhiko Ito
小嶋翔，伊藤治彦

Department of chemistry, Nagaoka University of Technorogy, Kamitomioka, Nagaoka 940-2188, Japan
長岡技術科学大学材料開発工学専攻　〒940-2188　新潟県長岡市上富岡町1603-1

Hydrogenated amorphous carbon nitride (a-CN_x:H) films with high nitrogen content were formed by the microwave discharge of the gas mixture of C_6H_6 and N_2. Compositional analysis was made by XPS which yields [N]/([N]+[C])=0.35−0.5. The CN($A^2\Pi_i$-$X^2\Sigma^+$) transition was observed with the laser induced fluorescence spectroscopy, and the number densities of the CN($X^2\Sigma^+$) state are evaluated as 4.9×10^{17}–7.2×10^{17} m^{-3}. A correlation between the CN($X^2\Sigma^+$) density and the [N]/([N]+[C]) ratio and the comparison of the ratio of the flux of N atoms incorporated into films and that of the gas-phase CN radicals with the sticking probability of CN radicals indicate the mechanism of the incorporation of N atoms.

1. Introduction

Amorphous carbon nitride (a-CN_x) films have been attracted much attention due to the expectation of their mechanical hardness [1]. This expectation is based on the shortness of the length (1.48 Å) of the C-N bonds compared with that (1.54 Å) of C-C in the sp^3 hybridized state [2]. Therefore, it has been the central problem in the field of the synthesis of a-CN_x to incorporate N atoms as much as possible. However, it is difficult to obtain high-N content by using the frequently-used method of the microwave (MW) discharge of the gas mixture of N_2 and hydrocarbons. Ito and co-workers have developed an alternative method to deposit a-CN_x films by using the decomposition of BrCN with the MW-discharge flow of Ar [3]. This reaction produces CN radicals almost selectively. They are the precursor of the film formation, leading to the high-N content ([N]/([N]+[C]) ≦ 0.5) of the resultant films. In this study, hydrogenated a-CN_x (a-CN_x:H) films are deposited by using the MW-discharge decomposition of C_6H_6 diluted with excess amount of N_2. In this reaction system, the source of N atoms of films has not been identified. In this study, the contribution of CN($X^2\Sigma^+$) radicals to the N source of films is evaluated based on the ratio, s, of the fluxes defined as

$$s=\Phi_{\text{a-CN}}/\Phi_{\text{CN(X)}}, \quad (1)$$

where $\Phi_{\text{a-CN}}$ is the flux of N atoms incorporated into films and $\Phi_{\text{CN(X)}}$ is that of CN radicals in the gas phase. In the case of the BrCN/Ar system stated above, s is the sticking probability of CN($X^2\Sigma^+$) radicals [3]. In eq. (1), $\Phi_{\text{CN(X)}}$ can be evaluated from the number density, $n_{\text{CN(X)}}$, of CN($X^2\Sigma^+$) radicals determined by using the laser-induced fluorescence (LIF) spectrum of the CN($A^2\Pi_i$-$X^2\Sigma^+$) transition and by the flow speed, V, in units of m s^{-1} as $n_{\text{CN(X)}}V$. $\Phi_{\text{a-CN}}$ can be evaluated from the mass of the N component of the film, w, the deposition time, t_d, and the area of the substrate, A, as wL/Mt_dA, where L and M are the Avogadro constant and the atomic mass of N, respectively.

2. Experimental

Fig. 1 shows the experimental arrangement for the deposition of a-CN_x films. A Si substrate was placed ≈1 cm downstream of the discharge tube. After the chamber was evacuated <1 mTorr, N_2 was introduced through a desiccant (P_2O_5) with the range of pressure (P_{N2}) of 0.2-0.4 Torr. Prior to the film deposition, MW discharge (2.45 GHz, 60 W) of N_2 was generated for 30 min. Then, C_6H_6 was introduced into the chamber through P_2O_5 with the partial pressure of 5 mTorr. Films were deposited for 1 h. After the deposition, films were analyzed by XPS and IR. In addition, The LIF spectrum of the CN($A^2\Pi_i$-$X^2\Sigma^+$), 4-0 band, was observed using a dye laser pumped by the 2-nd harmonic of a

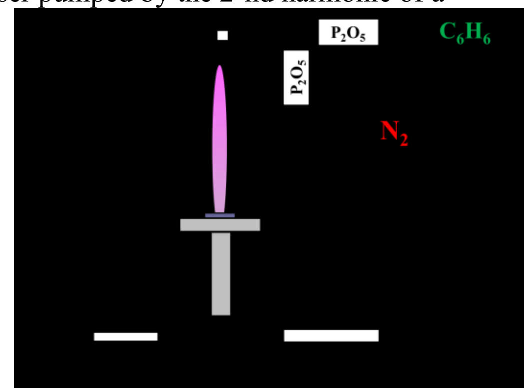

Fig. 1 MWCVD apparatus.

Nd:YAG laser. In this experiment, the Si substrate was not used and the dye-laser beam was introduced into the position of the Si substrate. V was evaluated from time-resolved emission measurements as follows. The experimental setup of this measurement was the same as described in ref. [3]. By modulating the MW discharge using a pulse generator, the delay between the emission signals of MW discharge of Ar in the upstream of the discharge tube and of the $CN(B^2\Sigma^+\text{-}X^2\Sigma^+)$ emission generated by the dissociative excitation of acetonitrile in the downstream of the discharge tube was monitored, and converted into V.

3. Result

Fig. 2 shows the observed LIF spectrum of the $CN(A^2\Pi_i\text{-}X^2\Sigma^+)$, 4-0 band (upper trace) and the result of simulation analysis (lower trace). The details of the analysis are the same as described in ref. [3]. From the simulation analysis, the intensity of the individual transition was evaluated which was calibrated against Rayleigh scattering intensity of Ar atoms to determine $n_{CN(X)}$. Table 1 shows the $n_{CN(X)}$ values together with the [N]/([N]+[C]) values of films determined by use of XPS analysis.

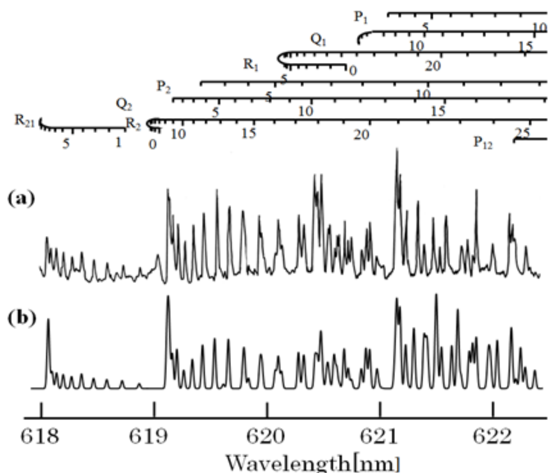

Fig. 2 CN $(A^2\Pi_i\text{-}X^2\Sigma^+)$, 4-0 band ($P_{N2}$= 0.4Torr).
(a) Observed. (b) Simulated.

Table 1 Number density and nitrogen content.

P_{N2}[Torr]	$n_{CN(X)}$ [m^{-3}]	[N]/([N]+[C])
0.2	4.9×10^{17}	0.33
0.3	7.2×10^{17}	0.45

Fig. 3 shows the results of the measurement of V. From the above results, the s values are determined as listed in Table 2 where the sticking probability of the CN radicals determined in our previous study [3] is also listed.

4. Discussion

From Table 1, a positive correlation was observed between $n_{CN(X)}$ and [N]/([N]+[C]). From Table 2, the s values for the C_6H_6/N_2 system are in good agreement with the sticking probability of CN radicals. From these observations, the dominant N source of films is identified as $CN(X^2\Sigma^+)$ radicals. The maximum value of the present s, 0.45, is higher than that of the sticking probability, 0.22. This observation indicates that the gas-phase nitrogen atoms may contribute to the N source of films as well as CN radicals under the high-P_{N2} conditions.

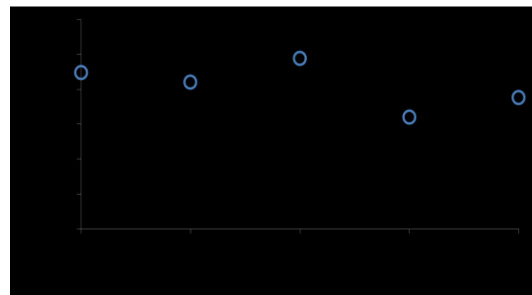

Fig. 3 Flow speed.

Table 2 Value of s and the sticking probability of CN radicals.

C_6H_6 / N_2 s value	sticking probability of CN radicals
0.11-0.45	0.11-0.22

5. Concluding remarks

Films of a-CN_x:H were deposited onto Si substrates using the MW-discharge of the gas mixture of C_6H_6 and N_2. By using excess amount of N_2 compared with C_6H_6, high [N]/([N]+[C]) ratios of 0.33−0.45 were obtained. According to the correlation between the [N]/([N]+[C]) ratio and the $CN(X^2\Sigma^+)$ density and to the comparison of the s values with the sticking probability of CN radicals, the nitrogen source of the present films is identified as CN radicals. The contribution of gas-phase N atoms is also indicated under the high-P_{N2} conditions.

References

[1] W. Kulisch, Deposition of Diamond-Like Superhard Materials, Springer-Verlag, Berlin, 1999
[2] J. R. Fuhr and W. L. Wiese, in: D. R. Lide (Ed.), CRC Handbook of Chemistry and Physics, CRC Press,Boca Raton, 1998, Chap. 9.
[3] H. Ito et al., Spectrochimica Acta A, **86** (2012) 256.