

## Precursors of a-CN<sub>x</sub>:H films from the decomposition of CH<sub>3</sub>CN with the microwave discharged products of Ar

Arのマイクロ波放電フローによるCH<sub>3</sub>CNの分解: a-CN<sub>x</sub>:H膜の前駆体

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The decomposition reaction of CH<sub>3</sub>CN induced by the microwave discharge flow of Ar was applied to the formation of hydrogenated amorphous carbon nitride (a-CN<sub>x</sub>:H) films. A discussion was developed whether CN(X<sup>2</sup>Σ<sup>+</sup>) radicals are the dominant source of N atoms of films based on the ratios of the fluxes  $\Phi_{a-CN}/\Phi_{CN(X)}$  evaluated for the cases of CH<sub>3</sub>CN and BrCN as the starting materials. The flux of CN(X<sup>2</sup>Σ<sup>+</sup>) radicals arrived onto the film surface,  $\Phi_{CN(X)}$ , was evaluated from the number density of CN(X<sup>2</sup>Σ<sup>+</sup>) radicals determined from the intensity of the laser-induced fluorescence spectrum of the CN(A<sup>2</sup>Π<sub>1</sub>-X<sup>2</sup>Σ<sup>+</sup>), 4-0 band together with the flow speed measured by the time-resolved emission. The flux of N atoms incorporated into films,  $\Phi_{a-CN}$ , was evaluated from the atomic composition analysis by XPS and the film mass. According to the discussions on the difference of the above ratios and on the electron densities in the reaction region, CN(X<sup>2</sup>Σ<sup>+</sup>) radicals are suggested to be the dominant N source of a-CN<sub>x</sub>:H films.

### 1. Introduction

Amorphous carbon nitride (a-CN<sub>x</sub>) films are formed by using the decompositions of BrCN and CH<sub>3</sub>CN with the microwave (MW) discharge flow of Ar. In the case of BrCN, CN radicals are formed almost selectively. Therefore, the main nitrogen source of a-CN<sub>x</sub> is CN(X<sup>2</sup>Σ<sup>+</sup>) radicals, and the sticking probability,  $s$ , of CN(X<sup>2</sup>Σ<sup>+</sup>) radicals can be determined with a simple scheme as [1-5]

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

In the case of the flowing-afterglow apparatus used in this study,  $\Phi_{CN(X)}$  can be evaluated from the number density of CN(X<sup>2</sup>Σ<sup>+</sup>) radicals,  $n_{CN(X)}$ , determined by using the laser-induced fluorescence (LIF) spectrum of the CN(A<sup>2</sup>Π<sub>1</sub>-X<sup>2</sup>Σ<sup>+</sup>) transition and the flow speed,  $V$ , in units of m s<sup>-1</sup>, as  $n_{CN(X)}V$ .  $\Phi_{a-CN}$  can be evaluated from the mass of the CN 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 molecular mass of CN, respectively. In the case of CH<sub>3</sub>CN, however, other radicals are suspected to contribute as the N source of films. In this paper, the  $s$  values obtained by using BrCN and CH<sub>3</sub>CN as the starting materials are represented as  $s_{BrCN}$  and  $s_{CH_3CN}$ , respectively. The following three cases may be possible.

(A) If the precursor of a-CN<sub>x</sub>:H in the case of CH<sub>3</sub>CN is specifically CN(X<sup>2</sup>Σ<sup>+</sup>) radicals,  $s_{CH_3CN}$  may be identical with  $s_{BrCN}$ .

(B) If other radicals contribute to the deposition of a-CN<sub>x</sub>:H in addition to CN(X<sup>2</sup>Σ<sup>+</sup>),  $s_{CH_3CN}$  may be larger than  $s_{BrCN}$ .

(C) If the rate of the surface recombination [6] of CN(X<sup>2</sup>Σ<sup>+</sup>) is higher in a-CN<sub>x</sub>:H films formed from CH<sub>3</sub>CN than that in a-CN<sub>x</sub> films formed from BrCN,  $s_{CH_3CN}$  may be smaller than  $s_{BrCN}$ .

Based on these considerations,  $s_{CH_3CN}$  is evaluated in this study, and is compared to  $s_{BrCN}$  to discuss the possibility that CN(X<sup>2</sup>Σ<sup>+</sup>) radicals are the dominant N source of a-CN<sub>x</sub>:H in the case of CH<sub>3</sub>CN.

### 2. Experiment

Fig. 1 shows the experimental arrangement for the deposition of a-CN<sub>x</sub> and a-CN<sub>x</sub>:H films. Ar (0.2-0.4 Torr) was excited by MW discharge (2.45 GHz, 60W). BrCN or CH<sub>3</sub>CN were introduced through a nozzle to deposit films on the Si substrates set just downstream (=10 mm) of the nozzle tip. The mass,  $W$ , of films were measured with the deposition time of  $t_d=1$  h. The LIF spectrum of the CN(A<sup>2</sup>Π<sub>1</sub>-X<sup>2</sup>Σ<sup>+</sup>), 4-0 band, was observed using a dye laser pumped by the 2-nd harmonic of a 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 a time-resolved emission measurements by modulating the MW discharge using a pluse generator. The compositional analysis was made by using XPS. The electro-static probe measurements were made in this study to evaluate the density,  $n_e$ , and the temperature,  $T_e$  of electrons.

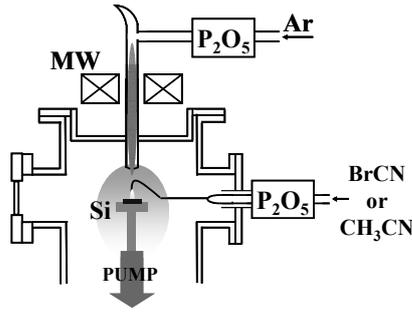


Fig. 1 Schematic of the MWCVD apparatus

### 3. Results and discussion

Fig. 2(a) shows the observed LIF spectrum of the  $\text{CN}(A^2\Pi_i-X^2\Sigma^+)$ , 4-0 band. A simulation analysis was made as shown in Fig. 2(b) to evaluate the intensity of the individual transition. This intensity was calibrated against Rayleigh scattering intensity of Ar, from which was evaluated the number density of the individual vibration-rotation levels of CN,  $n_{\text{CN}(X)}(\nu, J)$ . Then,  $n_{\text{CN}(X)}$  was evaluated as

$$n_{\text{CN}(X)} = \sum_{\nu, J} n_{\text{CN}(X)}(\nu, J) \quad (2)$$

The compositional analysis was made by using XPS as listed in Table 1. In addition to C and N, O and Br were detected. Then,  $w$  was determined from observed  $W$  by excluding the masses of O and Br and by assuming that all the N atoms form CN bonds. Fig. 3 shows the dependencies of  $s_{\text{CH}_3\text{CN}}$  and  $s_{\text{BrCN}}$  on  $n_e$ . The  $s_{\text{CH}_3\text{CN}}$  and  $s_{\text{BrCN}}$  values have negative dependencies on  $P_{\text{Ar}}$  irrespective of the experimental conditions. The  $s_{\text{CH}_3\text{CN}}$  values are in good agreement with  $s_{\text{BrCN}}$  obtained under the  $\text{H}_2\text{O}$ -added condition [5]. In addition, the  $n_e$  values obtained in the case of  $\text{CH}_3\text{CN}$  are almost identical with those obtained in the case of BrCN under the  $\text{H}_2\text{O}$ -added condition. These comparisons indicate that the  $s$  values depend strongly on  $n_e$  and that  $s_{\text{CH}_3\text{CN}}$  and  $s_{\text{BrCN}}$  are almost identical under the similar condition of  $n_e$ .

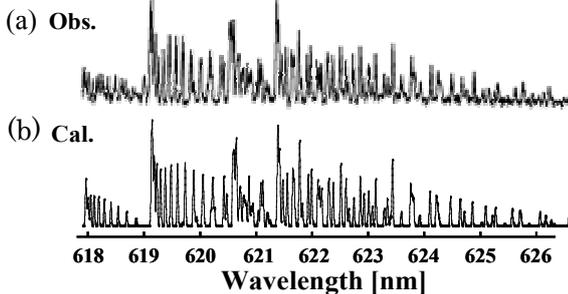


Fig. 2 LIF spectra of the  $\text{CN}(A^2\Pi_i-X^2\Sigma^+)$ , 4-0 band. (a) Observed. (b) Simulated.

Table 1 Compositional analysis

	C	N	O	Br	$[\text{N}]/([\text{N}]+[\text{C}])$
BrCN	41	31	34	5	0.43
$\text{CH}_3\text{CN}$	62	25	13	-	0.28

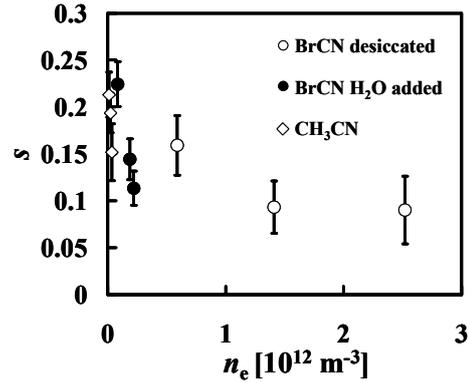


Fig. 3 Dependencies of  $s_{\text{CH}_3\text{CN}}$  and  $s_{\text{BrCN}}$  on  $n_e$

### 4. Conclusion

In this study, a novel method of analysis was developed to discuss whether  $\text{CN}(X^2\Sigma^+)$  radicals are the dominant N source of a- $\text{CN}_x\text{:H}$  films formed from the decomposition reaction of  $\text{CH}_3\text{CN}$  with the MW discharge products of Ar. The basic idea is the comparison of the ratios of the fluxes  $\Phi_{\text{a-CN}}/\Phi_{\text{CN}(X)}$  evaluated for the cases of  $\text{CH}_3\text{CN}$  and BrCN as the starting materials. The 4-0 band of the  $\text{CN}(A^2\Pi_i-X^2\Sigma^+)$  transition was observed by the LIF spectroscopic method, and the intensity of the transitions was calibrated against Rayleigh scattering intensity of Ar, yielding the number density of  $\text{CN}(X^2\Sigma^+)$  radicals. From these densities together with the flow speed measured by the time-resolved emission,  $\Phi_{\text{CN}(X)}$  was evaluated.  $\Phi_{\text{a-CN}}$  was evaluated from the atomic-composition analysis by XPS and the film mass. According to the discussions on the difference of the above ratios and on the electron densities of the reaction region,  $\text{CN}(X^2\Sigma^+)$  radicals are suggested to be the dominant N source of a- $\text{CN}_x\text{:H}$  films formed from the decomposition of  $\text{CH}_3\text{CN}$  induced by the MW plasma flow of Ar. From the above considerations, the case (A) described above may be applicable to the present  $s_{\text{CH}_3\text{CN}}$ .

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