A novel method was presented to analyze the contribution of CN radicals to the N source of hydrogenated amorphous carbon nitride films based on the ratio of the fluxes, $s = \Phi_{a-CN}/\Phi_{CN}$, where $\Phi_{a-CN}$ is the flux of N atoms deposited and $\Phi_{CN}$ is that of CN radicals. Films were formed by the microwave discharge of C$_6$H$_6$ vapor diluted with N$_2$. $\Phi_{CN}$ was evaluated from the density of CN radicals determined from the intensity analysis of the laser-induced fluorescence spectra of the CN($A^2\Pi_i - X^2\Sigma^+$) transition and the flow speed by a time-resolved emission measurement. $\Phi_{a-CN}$ was evaluated from the mass of a deposited film calibrated against the atomic compositions determined from the combination of Rutherford backscattering and elastic recoil detection measurements. From the comparison of the present $s$ values and the sticking probability of CN radicals determined in our previous study [Spectrochimica Acta PartA: Molecular and Biomolecular Spectroscopy, 86, 256-265 (2012)], CN radicals were found to be the origin of 30-50% of N atoms of films fabricated in the present reaction system.

Key words: hydrogenated amorphous carbon nitride, CN radicals, laser spectroscopy, sticking probability, deposition mechanism
We can evaluate $n_{\text{CN}}$ based on the LIF spectroscopy, $I$ on the time-resolved emission measurements, and $N_{\text{CN}}$ from the film mass, $w$, which is calibrated against the compositional analysis. Since the source of N atoms in the films formed from reaction (1) can be specified as CN radicals, the $s$ value for this reaction system (defined as $s_{\text{BrCN}}$ hereafter) is identical with the sticking probability of CN radicals. $s_{\text{BrCN}}$ has been evaluated to be in the range of 0.15-0.09 and 0.22-0.11 under the desiccated and H$_2$O-added conditions, respectively [10]. If the $s$ values are determined for other reaction systems, the comparison between $s$ and $s_{\text{BrCN}}$ may lead to the following cases. (A) If $s_{\text{BrCN}}$, the N source may be specifically CN radicals. (B) If $s > s_{\text{BrCN}}$, the other radicals may also contribute to the N source of films. In our previous study, we have successfully identified the source of N atoms of a-CN$_x$H$_y$ films formed from the decomposition of CH$_4$ and MW discharge flow of Ar as CN radicals [11]. In this study, we extend this method to the formation of a-CN$_x$H$_y$ films from the MW discharge flow of the gas mixture of N$_2$ and hydrocarbons. Preceding the present study, we have examined several hydrocarbon sources such as CH$_4$, C$_2$H$_2$, and C$_6$H$_6$. Among them, we have been able to obtain a high deposition rate for measuring $w$ when we choose C$_6$H$_6$.

2. EXPERIMENTS

Figure 1 shows the schematic diagram of the MW CVD apparatus used in this study, where the setup to observe the LIF spectrum is shown. A stainless-steel chamber with the outer diameter of 101.6 mm$^2$ was evacuated using mechanical-booster (95 m$^3$/h) and oil-rotary (670 L/min) pumps. N$_2$ (99.9998% purity) was introduced under the pressure ($P_{\text{N}_2}$) of 0.2–0.4 Torr through a quartz-glass discharge tube of 15 mm$^2$, and was excited by a MW discharge (2.45 GHz, 60 W). C$_6$H$_6$ was introduced into the upstream of the discharge section through a stainless-steel nozzle (1 mm$^2$). The partial pressure of C$_6$H$_6$ was 5 mTorr measured with a Penning vacuum gauge (ULVAC GI-PA). H$_2$O molecules included in N$_2$ and C$_6$H$_6$ as impurity and/or adsorbed on the wall of the apparatus were removed by passing through P$_2$O$_5$. We have evaluated the effect of the above desiccation procedure for the system of BrCN/Ar in the same experimental setup; the OH(A’$\Sigma^+$–X’$\Sigma^-$) emission intensity due to the dissociative excitation of impurity H$_2$O has decreased to $\approx$3% when the materials are passed through P$_2$O$_5$ [7].

The experimental setup to measure LIF is the same as described in refs. [9-11]. The 4–0 (618–625 nm) band of the CN(A’$\Pi$–X’$\Sigma^-$) transition was observed by using a pulsed dye laser (Quantel TDL-60) excited by the second harmonic of a Nd:YAG laser (Continuum Surelite I-10). The energy of the dye-laser beam was 3 mJ/pulse at which the LIF intensity was fully saturated. CN(X’$\Sigma^-$) radicals in the v=0 level were excited to the first-excited (A’$\Pi$) state in the v=4 level by the dye-laser beam where $v$ denotes the vibrational quantum number. Fluorescence from the A’$\Pi$ v=4 level was detected by a photomultiplier tube (PMT; Hamamatsu R955) through a quartz window (W), three lenses (L$_1$, L$_2$, and L$_3$), and a slit (S) shown in Fig. 1. A sharp-cut filter (F; HOYA Y52) was set in front of PMT. The signal from PMT was processed with two boxcar integrators A and B (Stanford Research Systems SR250). The sampling gate widths of A and B were set at 15 $\mu$s, and the delay of the sampling gate of B from that of A was set at 60 $\mu$s. The input signal of A consists of pulsed LIF and continuous emission signals and that of B of only the latter. Then, the difference of the output signals (A–B) was recorded to eliminate the integration of the emission signal.

Rayleigh scattering intensity, $I_R$, of N$_2$ was measured to calibrate the intensity of the LIF spectrum as follows. First, $I_R$ was observed with $P_{\text{N}_2}$ varying in the region of 0.2–0.6 Torr, where the wavelength of the dye laser was set at the R$_3$ head of the CN(A’$\Pi$–X’$\Sigma^-$), 4–0 band (618 nm). In this measurement, only an oil-rotary pump was used for evacuation to prevent a pressure gradient in the observation region. It was confirmed that the “observed” $I_R$ was proportional to $P_{\text{N}_2}$ with slight positive intercept at $P_{\text{N}_2}=0.0$ Torr. Then, the difference between the “observed” $I_R$ at $P_{\text{N}_2}$=0.4 Torr and the intercept was used for the calibration of LIF intensity.

The experiment to determine $F$ was made as described in ref. [10] where reaction (1) was used. Ar was introduced into the discharge tube, and BrCN was introduced through a nozzle set just upstream of the laser-beam path. The MW discharge was pulsed by using the digital delay generator (PG, Stanford DG535) with the repetition and the width of 10 Hz and 0.1 ms, respectively. Emission signal from the MW discharge of Ar was monitored using a PMT set just upstream of the MW cavity, and that from the CN(B’$\Sigma^+$–X’$\Sigma^-$) emission was monitored by the same PMT as shown in Fig. 1. The emission signals from two PMT’s were stored into a digital oscilloscope (Lecroy LT372) triggered by the TTL pulses from PG. Then, the time interval between the outputs from two PMT’s was measured and was converted to $F$.

Films were deposited onto Si substrates set at the same set as that of the laser-beam path. The laser was not fired in this experiment. Prior to the deposition, the surface of a substrate was exposed to the N$_2$ plasma for 1 h for cleaning. Then, C$_6$H$_6$ was introduced to deposit film ($t_0=1$ h) to measure $w$.

The atomic compositions of films were measured using the combination of Rutherford backscattering (RBS) and elastic recoil detection analysis (ERDA) using an electrostatic accelerator (Nisshin-High Voltage NT-1700HS) located at Extreme Energy-Density Research Institute of Nagaoka University of Technology. Films were irradiated with He$^{+}$ beam accelerated to 25 MeV. In RBS measurement, scattered beam was detected by a solid-state detector (SSD). The
irradiation and detection angles of He\(^{2+}\) beam were 18° and 78°, respectively, from the film surface. In the ERDA measurement, recoiled H atoms were detected with another SSD positioned at an angle of 168° from the film surface.

3. RESULTS

Figure 2(a) shows the observed LIF spectrum of the CN(A\(^{2}Π\)–X\(^{2}Σ\)) 4–0 band taken under the condition of \(P_{\text{N}_2} = 0.3 \text{ Torr}\). The assignments of the spectral lines were confirmed based on ref. [12]. Since each spectral line in Fig. 2(a) consisted of several overlapping transitions, the relative intensity, \(I_{\nu',\nu} / I_{0}\), for the individual transition was quoted from ref. [12]. Since each spectral line in Fig. 2(b) was attributed to the CN(A\(^{2}Π\)) 4–0 band taken under the condition of \(P_{\text{N}_2} = 0.3 \text{ Torr}\), the effective lifetime of the CN(A\(^{2}Π\)) state is represented as \(\tau_{\text{eff}}\) [13]. \(S_{\text{eff}}(J)\) is the sensitivity of the LIF detection system. \(I_{\text{R}}\) can be represented as [15]

\[
I_{\text{R}} = n_{\text{N}_2}E_{\text{p}}\frac{\partial \sigma_{\text{eff}}}{\partial \omega}S_{\text{eff}}(\lambda_{\text{R}})L, \tag{6}
\]

where \(n_{\text{N}_2}\) is the number density of N\(_2\) under the condition of \(P_{\text{N}_2} = 0.4 \text{ Torr}\), \(E_{\text{p}}\) is the energy of the laser pulse, \(\partial \sigma_{\text{eff}}/\partial \omega\) is the differential cross section of Rayleigh scattering of N\(_2\) [16], and \(S_{\text{eff}}(\lambda_{\text{R}})\) is the sensitivity of the detection at the wavelength \(\lambda_{\text{R}}\) of Rayleigh scattering. According to eqs. (5) and (6), \(n_{\text{CN(X)}}\) was evaluated, and they are summed up to determine \(n_{\text{CN(X)}}\) as

\[
n_{\text{CN(X)}} = \sum_{\nu'\nu} n_{\nu'\nu}. \tag{7}
\]

The \(n_{\text{CN(X)}}\) values obtained under the various experimental conditions are listed in Table I. The errors in \(n_{\text{CN(X)}}\) are ±10–20% from those in \(I_{\text{R}}\). Table I also lists the values of \(V\) and \(w/A\) measured as described in section 2. The summation on \(\nu'\) was not taken as follows. We observed the 5–1 band appearing in the region of 632–639 nm under the condition of \(P_{\text{N}_2} = 0.3 \text{ Torr}\). The value of \(\sum n_{\nu'\nu}\) yielded to be \(8 \times 10^{16} \text{ m}^{-2}\), which was comparable with the uncertainty in \(n_{\text{CN(X)}}\). Therefore, the contribution of \(\nu'=1\) was negligible.

Table II lists the results of the compositional analysis of films. H, C, and N atoms are the main components. The origin of the impurity O atoms may be in H\(_2\)O molecules remaining in the reaction region or from the atmosphere during the waiting time (several days) of the compositional analysis. The [N]/([N]+[C]) ratios are 0.39–0.50 as listed in Table II which are unexpectedly large.

4. DISCUSSION

Figure 4 shows the \(s\) values evaluated by substituting

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Fig. 2 The 4–0 band of the CN(A\(^{2}Π\)–X\(^{2}Σ\)) transition taken under the condition of \(P_{\text{N}_2} = 0.3 \text{ Torr}\). (a) Observed. (b) Calculated.

Fig. 3 Intensity distribution of the CN(A\(^{2}Π\)–X\(^{2}Σ\)) 4–0 band under the condition of \(P_{\text{N}_2} = 0.3 \text{ Torr}\).
the observed values listed in Tables I and II to eqs. (2)-(4) together with those evaluated for the BrCN/Ar [10] and CH3CN/Ar [11] systems. In Fig. 4, the horizontal axis represents $P_{N2}$ in the C6H6/N2 system and the pressure of Ar, $P_{Ar}$, in the BrCN/Ar and CH3CN/Ar systems. The present $s$ values are systematically larger than those for the previous values ($s_{BrCN}$), indicating that the case (B) described in section 1 can be applicable in the present reaction system. According to the comparison between the present $s$ values and $s_{BrCN}$ shown in Fig. 4, CN radicals may contribute to 35-50% of N atoms of films in the C6H6/N2 system.

In the following discussion, the rest of the N source can be specified as gas-phase N atoms based on the kinetic analysis. N2 may dissociate into N atoms via electron impact induced by the MW discharge. The rate constant of this process was evaluated from the reported cross section [17] and the electron temperature measurement for reaction (1) [8] to be $2\times10^{-15}$ m$^3$s$^{-1}$. The loss process of N atoms may be the reaction with C6H6 molecules whose rate constant is very small $<6.6\times10^{-21}$ m$^3$s$^{-1}$ [18]. Then, the steady-state condition of these processes yields the number density of N atoms to be $>6\times10^{18}$ m$^{-3}$. The flux of N atoms incorporated into films may be evaluated to be $>1\times10^{19}$ m$^{-2}$s$^{-1}$ using the reported sticking probability of N atoms, 0.0041 [17], and the flow speed listed in Table I. On the other hand, the flux of CN radicals incorporated is evaluated from Table I as $2\times10^{19}$ m$^{-2}$s$^{-1}$. Therefore, the contribution of N atoms to the N source of films is comparable with that of CN radicals. In conclusion, CN radicals and N atoms are the dominant N sources of a-CN$_x$H$_y$ films fabricated in this study.

5. CONCLUSION
A-CN$_x$H$_y$ films have been fabricated using the MW discharge of C6H6 diluted with N2, and the contribution of CN radicals to the N source of films has been analyzed by comparing $s$ with $s_{BrCN}$ determined previously [10]. CN radicals have been found as the origin of 35-50% of N atoms of films. A simple kinetic analysis has revealed that the rest of N atoms of films may come from the gas-phase N atoms produced by the MW discharge of N2. The precursors of the film deposition in the present reaction system may then be hydrocarbon radicals, CN radicals, and N atoms. According to the experimental configuration shown in Fig. 1, hydrocarbon radicals may deposit predominantly onto the wall of the quartz discharge tube; the concentration of these radicals may drop largely in the film-deposition region, leading to higher [N]/([N]+[C]) ratios (see Table II) than in the literatures [4-6].

![Fig. 4 The $s$ values obtained for various reaction systems.](image)

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