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Laser Spectroscopy of CN Radicals in the Discharge Flow of the Gas Mixture of N_2 and Organic Vapor

N_2と有機化合物蒸気の混合気体放電フローで生成するCNラジカルのレーザー分光測定

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Hydrogenated amorphous carbon nitride (a-CN_x:H) films were formed from the microwave (MW) discharge of C_2H_2 or CH_3CN with the excess amount of N_2. The discussion was made whether $CN(X^2\Sigma^+)$ radicals were the main N source of the films or not on the basis of the ratio, s, of the fluxes of N atoms incorporated into films and of $CN(X^2\Sigma^+)$ radicals in the gas phase. The pressure of N_2 was in the range of 0.2-0.4 Torr and excited MW discharge (2.45GHz, 60W). The partial pressure of C_2H_2 or CH_3CN was 7 mTorr. The $CN(A^2\Pi_i$-$X^2\Sigma^+)$, 4-0 band was observed by the laser-induced fluorescence spectroscopy. The s values obtained both for C_2H_2 and CH_3CN were close to the reported sticking probability of $CN(X^2\Sigma^+)$ radicals. Therefore, it was suggested that $CN(X^2\Sigma^+)$ radicals were the main N source of the films.

1. Introduction

Hydrogenated amorphous carbon nitride (a-CN_x:H) films with high nitrogen content have been formed from the microwave (MW) discharge of C_2H_2 or CH_3CN with the excess amount of N_2 [1]. However, the source of the N atoms in these films has not yet been identified. On the other hand, it has been reported that $CN(X^2\Sigma^+)$ radicals are the dominant nitrogen source for the a-CN_x films formed by the decomposition reaction of BrCN by the MW discharge flow of Ar, and the sticking probability of $CN(X^2\Sigma^+)$ radicals has been determined [2]. This study reports on the main N source of films formed from C_2H_2/N_2 and CH_3CN/N_2 systems on the basis of the method as described below. The discussion was based on the s value defined as the ratio of the fluxes of N atoms incorporated into films and of the $CN(X^2\Sigma^+)$ radicals in the gas phase expressed as

$$s = N_{\text{a-CN}} / n_{\text{CN(X)}} V t_{\text{d}} A.$$

In the equation, $N_{\text{a-CN}}$ is the number of the N atoms incorporated into films, $n_{\text{CN(X)}}$ is the number density of $CN(X^2\Sigma^+)$ radicals, V is the flow speed, t_{d} is deposition time, A is the area of the substrate. When BrCN is used as the raw material, s is identical with the sticking probability of $CN(X^2\Sigma^+)$ radicals. Therefore, $CN(X^2\Sigma^+)$ radicals are the main nitrogen source of the present films if s is close to the sticking probability of $CN(X^2\Sigma^+)$. The other nitrogen-containing radicals may also contribute, if s is larger than the sticking probability of $CN(X^2\Sigma^+)$.

2. Experiment

Fig. 1 shows the experimental arrangement for the deposition of a-CN_x:H films. A Si substrate was set downstream (=10 mm) of the tip of the discharge tube. N_2 gas was introduced through P_2O_5 as the desiccant, and by a MW discharge (2.45 GHz, 60 W). The pressure of N_2 , P_{N2}, was in the range of 0.2-0.4 Torr. Trace amount of C_2H_2 or CH_3CN with the partial pressure of 7 mTorr was introduced through P_2O_5 in the upper part of the discharge tube. The deposition time was 30 min. The compositional

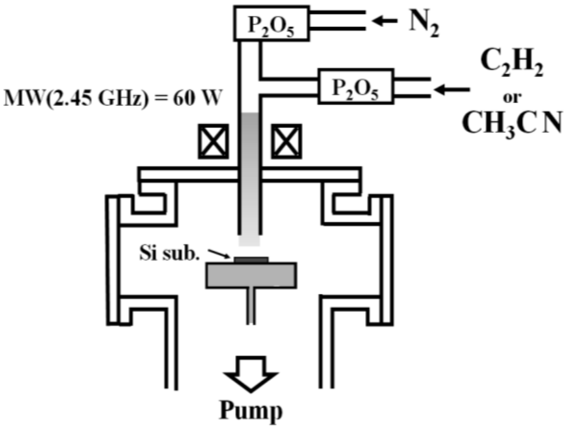

Fig. 1 schematic diagram of MW CVD apparatus analysis was made by using X-ray photoelectron spectroscopy (XPS) (JEOL, JPS-9010). The LIF spectrum of the CN($A^2\Pi_i$-$X^2\Sigma^+$), 4-0 band was observed by using a dye laser (Quantel TDL60) pumped by the 2-nd harmonic of a Nd:YAG laser (Continuum Surelite I-10) that passed downstream (=10 mm) of the tip of the discharge tube. In this experiment, the substrate stage was removed. The flow speed was measured by the time-resolved emission measurements using the dissociative excitation of BrCN with MW plasma of Ar, because the N_2 plasma did not fully extend into the observation region.

3. Results and discussion

Fig. 2(a) shows the observed LIF spectrum of the CN($A^2\Pi_i$-$X^2\Sigma^+$), 4-0 band under the condition of P_{N2}=0.4 Torr. 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 N_2, from which was evaluated the number density of the individual vibration-rotation levels of CN, n_{vJ}. Then, $n_{CN(X)}$ was given in the following expressions.

$$n_{CN(X)} = \sum_{v,J} n_{vJ}$$

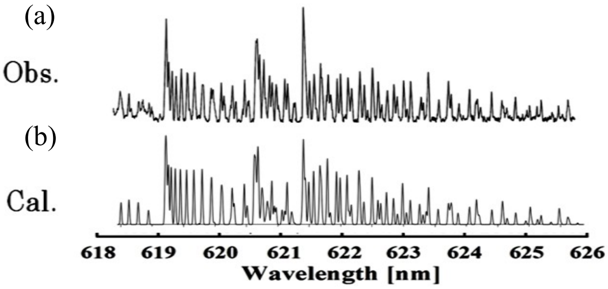

Fig. 2 LIF spectra of the CN($A^2\Pi_i$-$X^2\Sigma^+$), 4-0 band under the condition of P_{N2}=0.4 Torr.
(a) Observed. (b) simulated.

Table 1 shows the flow speed of Ar plasma. The difference of the flow speed between N_2 and Ar was negligible because there is no great difference in the density and the viscosity.

Table 1. The flow speed of Ar

Pressure of Ar [Torr]	Flow speed [m/s]
0.2	354
0.25	393
0.3	424
0.35	439
0.4	465

Fig. 3 shows the *s* values of C_2H_2/N_2, CH_3CN/N_2, BrCN/Ar, and BrCN/Ar obtained under the H_2O-added condition [2]. They have negative dependencies on P_{N2}. The *s* values determined in this study are in good agreement with the sticking probability of CN($X^2\Sigma^+$) under the H_2O-added condition. Therefore, it is suggested that the CN($X^2\Sigma^+$) radicals are the main N source of the present films. The reason for the sharp decrease in the *s* values under the conditions of 0.35-0.4 Torr is thought to be the convection.

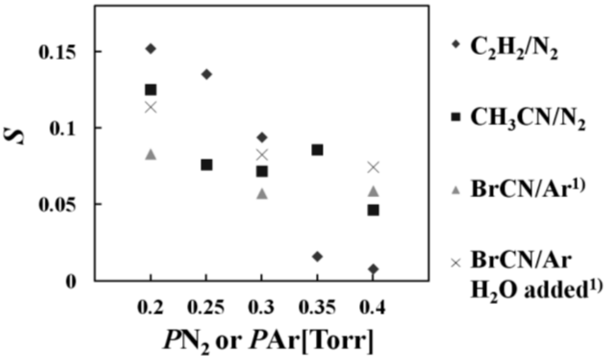

Fig.3 The *s* values for the individual condition

4. Conclusion

In this study, a novel method of analysis was developed to discuss whether CN($X^2\Sigma^+$) radicals are the dominant N source of a-CN_x:H films formed from the decomposition reactions of C_2H_2 and CH_3CN in the MW discharge of N_2. The basic idea is the comparison of the *s* values for the C_2H_2/N_2, CH_3CN/N_2, and BrCN/Ar systems. The intensity of the CN($A^2\Pi_i$-$X^2\Sigma^+$), 4-0 band was observed and calibrated against Rayleigh scattering intensity of N_2, yielding the number density of CN($X^2\Sigma^+$) radicals. The flow speed was measured by the time-resolved emission. $N_{a\text{-}CN}$ was evaluated from the atomic-composition analysis by XPS and the film mass. As a result, the *s* values obtained for these systems were close together. Accordingly, CN($X^2\Sigma^+$) radicals are suggested to be the dominant N source of a-CN_x:H films formed from the decomposition of C_2H_2 and CH_3CN induced by the MW plasma of N_2.

References

[1] H. Ito, H. Tsudome, and A. Kojima, IUMRS-ICA2014, A10-P28-001.

[2] H. Ito, H. Araki, A. Wada, A. Yamamoto, T. Suzuki, and H. Saitoh, Spectrochimica Acta Part A **86** 256 (2012).