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Fabrication of a-CN_x films by plasma decomposition of BrCN
BrCN の放電分解による a-CN_x 薄膜の形成

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Amorphous carbon nitride (a-CN_x) films with high nitrogen content ([N]/([N]+[C])=0.35−0.5) are formed by the RF discharge of the gas mixture of BrCN, Ar and N_2. Compositional analysis was made by XPS. The CN($B^2\Sigma^+-X^2\Sigma^+$) emission spectra were observed. A correlation between the emission intensity and the [N] / ([N] + [C]) ratio indicates the mechanism of the incorporation of N atoms when N_2 is introduced.

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 RF 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 microwave discharge flow of Ar [3]. This reaction produces efficiently CN radicals which become the precursor of the film formation, leading to the high-N content ([N]/([N]+[C])≦ 0.5) of the resultant films [4]. In this study, a-CN_x films are deposited by using the RF-plasma decomposition of BrCN diluted with Ar. In this reaction system, it is suspected that CN radicals may be further decomposed into C and N atoms. This “excess decomposition” may lead to the lowering of the [N]/([N]+[C]) ratio below 0.5, because the sticking probability of N atoms is quite small, 0.0041 [5]. In this experiment, N_2 was added to the reaction system to “compensate” the N content of films. The observation on the CN($B^2\Sigma^+-X^2\Sigma^+$) emission spectra was made to discuss the mechanism of this “compensation of N atoms” .

2. Experimental

Fig. 1 shows the experimental arrangement for the deposition of a-CN_x films. Si substrates were placed on the centers of the RF and grounded electrodes. After the chamber was evacuated <3 mTorr, Ar (0.1 Torr) was introduced through a desiccant (P_2O_5). Prior to the film deposition, RF plasma of Ar was generated for 4 h. Then, BrCN and N_2 were introduced into the chamber through P_2O_5. Films were deposited for 2 h. The partial pressures of Ar and N_2 (P_{Ar} and P_{N2}, respectively) were in the range of 0.0−0.3 Torr where the total pressure was kept constant to 0.3 Torr. After the deposition, films were analyzed by XPS, Raman, and IR. The optical emission spectra of the CN ($B^2\Sigma^+-X^2\Sigma^+$) transition were observed.

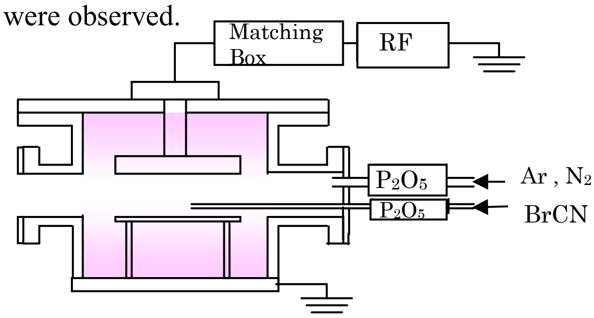

Fig.1 RF-plasma CVD apparatus

3. Results and discussion

The results of the compositional analysis using XPS are listed in Tables 1 and 2. According to these results, nitrogen content of the films were increased by introducing N_2.

Table 1 Compositional analysis (Grounded electrode)

Ar [Torr]	N_2 [Torr]	C	N	O	Br
0.3	0	54	30	10	6
0.2	0.1	44	35	13	8
0.1	0.2	41	41	13	5
0	0.3	46	39	10	5

Table 2 Compositional analysis (RF-electrode)

Ar [Torr]	N_2 [Torr]	C	N	O	Br
0.3	0	55	25	14	6
0.2	0.1	48	35	10	7
0.1	0.2	43	42	10	5
0	0.3	51	36	6	7

Fig. 2 shows the variation of the [N]/([N]+[C]) ratio as a function of P_{N2}. The ratio was ≈0.35 under the condition that N_2 was not introduced. When P_{N2} was increased, the [N]/([N]+[C]) ratio increased. This ratio became the maximum (≈0.5) under the condition of P_{N2}=0.2 Torr. The ratio dropped to 0.45 when Ar was not introduced.

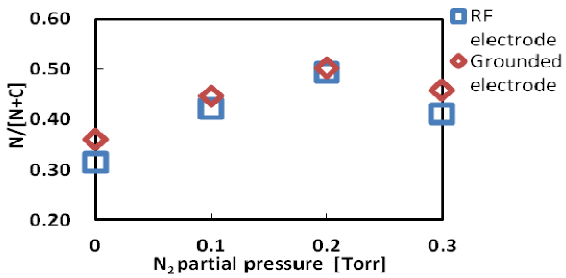

Fig. 2 Change of the nitrogen content as a function of P_{N2}

Fig. 3 shows the emission spectrum of the $CN(B^2\Sigma^+-X^2\Sigma^+)$ transition under the condition of P_{Ar}=0.1 Torr and P_{N2}=0.2 Torr. Fig. 4 shows the variation of the intensity of the $CN(B^2\Sigma^+-X^2\Sigma^+)$ emission spectrum as a function of P_{N2}. In this figure the intensity observed for P_{N2}=0.3 Torr was normalized to 1. As shown in Fig. 4, the highest emission intensity was observed under the condition of P_{N2}=0.2 Torr.

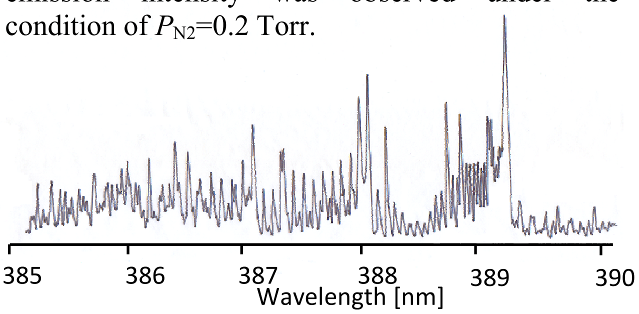

Fig. 3 Emission spectrum of the $CN(B^2\Sigma^+-X^2\Sigma^+)$ transition

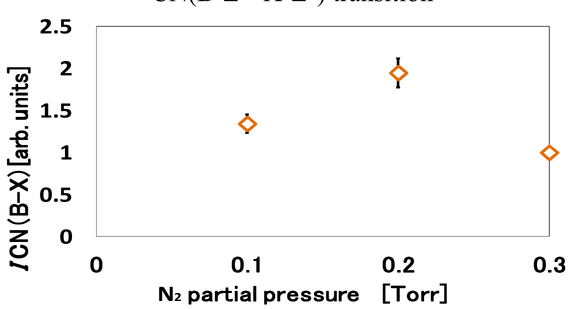

Fig. 4 Variation of the $CN(B^2\Sigma^+-X^2\Sigma^+)$ emission intensity as a function of P_{N2}

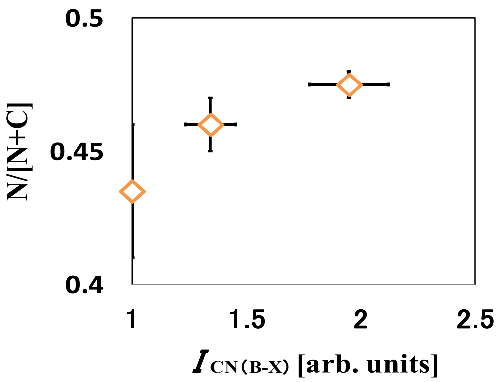

Fig. 5 Nitrogen content vs. emission intensity

Fig. 5 shows the variation of the nitrogen content as a function of the emission intensity. From Fig. 5, a strong correlation was observed between the emission intensity and the nitrogen content. The result shown in Fig. 5 indicates that CN radicals are the main source of nitrogen of films even under the condition of introducing N_2. Accordingly the mechanism of the "compensation of N atoms" in the films may be that C atoms produced via the "excess decomposition" of BrCN react with the discharged product of N_2 to form CN radicals which deposit to form a-CN_x with [N]/([N]+[C]) ≈0.5.

4. Concluding remarks

Films of a-CN_x were deposited onto Si substrates using the RF plasma excitation of the gas mixture of BrCN and Ar. By introducing N_2 into the reaction region, the N contents of films were controlled as 0.35−0.5; films formed under the condition of P_{Ar}=0.1 Torr and P_{N2}=0.1 Torr has the highest [N]/([N]+[C]) (=0.5). According to the correlation between the [N]/([N]+[C]) ratio of films and the $CN(B^2\Sigma^+-X^2\Sigma^+)$ emission intensity, the effect of the N_2 addition was elucidated; the discharged products of N_2 react with C atoms produced via the "excess decomposition" of BrCN to form CN radicals which becomes the precursor of the film formation.

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