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Analysis of dissociative excitation reactions of CH_3CN with the ECR plasmas of Ar and He

ArとHeのECRプラズマを用いたCH_3CNの解離励起反応解析

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The dissociative excitation reactions of CH_3CN with the electron-cyclotron resonance (ECR) plasmas of Ar and He were studied based on the electrostatic-probe measurements and on the optical emission spectra of the CN($B^2\Sigma^+$–$X^2\Sigma^+$) transition. The density and the temperature of free electrons and the CN($B^2\Sigma^+$–$X^2\Sigma^+$) emission intensity in these plasmas are varied by adding trace amount of H_2O. Based on a kinetic analysis, the decomposition of CH_3CN proceeds, predominantly, *via* the electron impact in the Ar plasma and *via* the electron impact and/or the ion-electron recombination in the He plasma. These results are found to be consistent with the evaluation of the number densities of CN($B^2\Sigma^+$) using the steady-state method. In addition, the compositional analysis of hydrogenated amorphous carbon nitride (a-CN_x:H) films prepared by the decomposition of CH_3CN in the ECR plasmas of Ar and He were carried out, yielding the [N]/([N]+[C]) ratios of 0.22 and 0.25, respectively.

1. Introduction

The dissociative excitation reactions of CH_3CN with microwave discharge of rare gass flows have been known to produce CN radicals with high efficiency, and strong emission spectra of the CN($B^2\Sigma^+$–$X^2\Sigma^+$) transition have been observed [1]. We have applied these reactions to the synthesis of hydrogenated amorphous carbon nitride (a-CN_x:H) thin films [2].

In the present study, the dissociative excitation mechanisms of CH_3CN in the electron-cyclotron resonance (ECR) plasmas of Ar and He were studied based on the electrostatic-probe measurements and on the optical emission spectra of the CN($B^2\Sigma^+$–$X^2\Sigma^+$) transition.

First, the dependencies of the CN($B^2\Sigma^+$–$X^2\Sigma^+$) emission intensity and the electron-energy distribution on the pressure of H_2O added to the ECR plasma flows of Ar and He were analyzed. Second, the formation rates of CN($B^2\Sigma^+$) state were evaluated by using the rate constants for the relevant reactions of the other molecules. Based on these results, the dissociative excitation processes of CH_3CN to produce the CN($B^2\Sigma^+$) state were clarified. In addition, a-CN_x:H films were deposited, and a compositional analysis of these films was carried out.

2. Experiments

The ECR plasma CVD apparatus was used. After the chamber was evacuated <10^{-4} Torr, Ar or He (2 mTorr) was introduced through a desiccant (P_2O_5). Then, microwaves (2.45 GHz, 70 W) were introduced into the chamber. H_2O molecules adsorbed on the wall of the chamber were removed by discharging Ar or He for 2 h. CH_3CN (1 mTorr) was introduced through P_2O_5. H_2O (0-0.6 mTorr) was introduced into the flow of CH_3CN.

The *I-V* characteristics were measured using the electrostatic-probe method to evaluate the density, n_e, and the temperature, T_e, of electrons. The optical emission spectra of the CN($B^2\Sigma^+$–$X^2\Sigma^+$) transition were measured.

Films of a-CN_x:H were formed for the Ar and He plasmas. In this experiment, the partial pressures of Ar or He and CH_3CN were 3 and 1 mTorr, respectively, where H_2O was not introduced. The atomic composition was obtained using X-ray photoelectron spectroscopy (XPS). Films deposited onto Si substrates of ≈7 mm^2 were used as the samples, for which the XPS measurements were carried out under the condition of 2.0×10^{-7} Pa (1.5×10^{-9} Torr) using a MgK_α source.

3. Results and discussion

The relative value of the emission intensity, I_{obs}, of the CN($B^2\Sigma^+$–$X^2\Sigma^+$) transition was plotted against P_{H2O} as shown by circles in Figs.1(a) and 1(b) for Ar and He, respectively. The electron density with the specific kinetic energy, $N_e(E_e)$,

$$N_e(E_e) = 2n_e(E_e/\pi)^{1/2}(kT_e)^{-3/2}\exp(-E_e/kT_e) \quad (1)$$

was evaluated from n_e and T_e. The emission intensity of the CN($B^2\Sigma^+$–$X^2\Sigma^+$) transition, I_{EI} and I_{Rec}, assuming the impact of high energy electrons and the charge transfer followed by the ion-electron recombination are expressed, respectively, as

$$I_{EI} \propto \int_{8.9\ eV}^{30\ eV} E_e^{1/2} N_e(E_e) dE_e \quad (2)$$

$$I_{Rec} \propto \int_{0\ eV}^{12.1\ eV} E_e^{1/2} N_e(E_e) dE_e. \quad (3)$$

Eqs. (2) and (3) were evaluated numerically and normalized at P_{H2O}=0 mTorr, and the results are shown by triangles and squares, respectively, in Figs.1(a) and 1(b). As shown in Fig.1(a), the observed values of the Ar plasma are in good agreement with the evaluations assuming electron impact. Therefore, the dominant process of production of CN($B^2\Sigma^+$) radicals is the electron impact in the ECR plasma of Ar. On the other hand, the two processes can not be distinguished in the case of He. In order to confirm the above findings, the number densities of CN($B^2\Sigma^+$) assuming electron impact and the ion-electron recombination, n_{EI} and n_{Rec}, were evaluated by the steady-state method. Table 1 lists the n_{EI} and n_{Rec} values for the Ar and He plasmas. The n_{EI} value for Ar was about three times larger than n_{Rec}. In the case of the He plasma, n_{EI} and n_{Rec} were almost identical. These evaluations are consistent with the conclusion derived from Figs. 1(a) and 1(b).

Table 2 shows the compositional analysis of a-CN_x:H films prepared by the decomposition of CH_3CN in the ECR plasmas of Ar and He, from which the [N]/([N]+[C]) ratios yielded to be 0.22 and 0.25, respectively. C and N atoms may originate in the starting material as expected. O atoms are presumably due to the atmospheric H_2O molecules adsorbed during the waiting time (several days) of the XPS measurement.

4. Conclusion

In the present study, the mechanism of dissociative excitation of CH_3CN to produce CN($B^2\Sigma^+$) radicals in the ECR plasmas of Ar and He was studied. In conclusion, the dissociation proceeds, predominantly, *via* the electron impact in the Ar plasma, and *via* the electron impact and/or the ion-electron recombination in the He plasma. The method employed in this study is possible to elucidate the decomposition mechanism of starting materials from the results of the optical emission measurements.

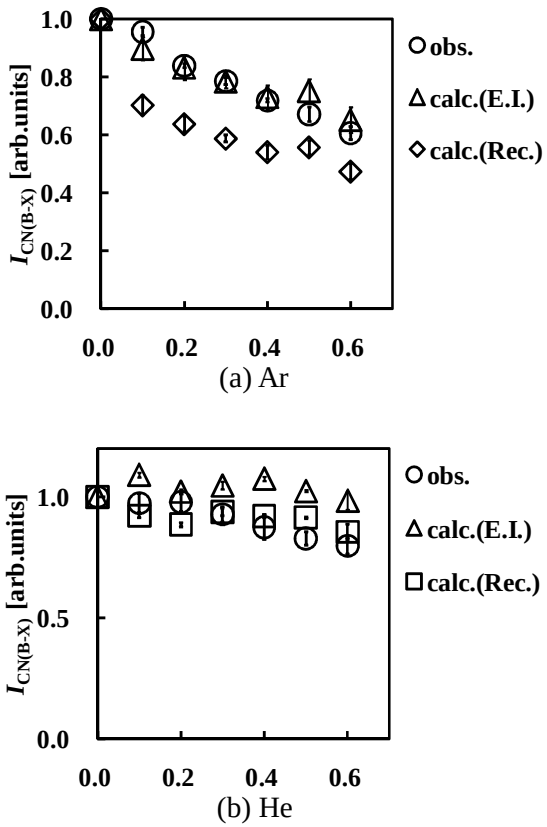

Fig.1 P_{H2O} dependencies of emission intensities

Table 1 The number densities of CN(B) (in units of 10^9 m^{-3})

	n_{EI}	n_{Rec}
Ar	7.41	2.58
He	6.39	5.96

Table 2 Compositional analysis of a-CN_x:H film prepared in the Ar and He plasmas.

	C [at%]	N [at%]	O [at%]	[N]/([N]+[C])
Ar	72.7	20.1	7.3	0.22
He	64.4	21.0	14.6	0.25

References

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