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Measurements of density and sticking probability of $CN(X^2\Sigma^+)$ radicals by laser-induced fluorescence spectroscopy

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Abstract

$CN(X^2\Sigma^+)$ radicals were produced by the decomposition of BrCN with the microwave discharge flow of Ar under the conditions of Ar pressure in the range of 0.40–0.70 Torr. The laser-induced fluorescence (LIF) spectra of the $CN(A^2\Pi_i–X^2\Sigma^+)$, 4–0, 5–1, and 7–2 bands were observed, and their intensities were calibrated against Rayleigh-scattering intensity by Ar atoms, from which the $CN(X^2\Sigma^+)$ radical density ($n_{CN(X)}$) was determined as $(0.67 \pm 0.25) \times 10^{18}$ to $(4.42 \pm 0.83) \times 10^{18}\,m^{-3}$. Hydrogenated amorphous carbon nitride (a-CN_x:H) films were formed by depositing the $CN(X^2\Sigma^+)$ radicals on Si substrates in the same reaction system as LIF. The sticking probability (s) of the $CN(X^2\Sigma^+)$ radicals onto the a-CN_x:H films was determined by using $n_{CN(X)}$, the flow speed, and the weight (w) of a-CN_x:H. The s value was determined as $(6.4 \pm 6.4) \times 10^{-2}$ to $(2.5 \pm 1.2) \times 10^{-2}$, where the errors are predominantly determined by those in $n_{CN(X)}$ and w. The procedure described in the present study will provide a methodology to determine the sticking probability of the precursor radicals of the film formation based on the gas-phase LIF spectroscopy.
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1. Introduction

Free radicals are known to play central roles in the plasma technology, because they are reactive intermediates and/or precursors of the film formation in plasma-enhanced chemical-vapor deposition (CVD) processes [1]. In these processes, free radicals are generated by the decomposition of gas-phase materials in discharge plasma; they react with other molecules and radicals to produce precursor radicals that deposit onto substrate. Therefore, detection of free radicals by spectroscopic method is crucial to analyze the chemical processes occurring in the plasma [2]. In particular, laser-induced fluorescence (LIF) spectroscopy of the electronic transitions of free radicals using a wavelength-tunable dye laser is one of the most sensitive methods of detection of them.

In this paper, we describe the LIF detection of the $CN(X^2\Sigma^+)$ radicals which are the precursor of the formation of amorphous carbon nitride (a-CN_x) films. The a-CN_x films have attracted much attention since they are expected to have high hardness [3]. This expectation is based on the shortness of their C–N bond (1.47 Å) compared with the sp^3-hybridized C–C bond (1.54 Å) [4]. Therefore, the development of a methodology for incorporating nitrogen atoms effectively into a-CN_x has been the central problem in their synthesis. One of the most widely used methods of forming a-CN_x films has been plasma-enhanced CVD of gas mixtures of hydrocarbon (mainly CH_4) and N_2; in this method, carbon and nitrogen precursors are produced separately and they react to form the CN bond on the substrate surface [5–8]. However, it is difficult to obtain high nitrogen content; the [N]/([N] + [C]) ratios of films have been limited to 0.2 at most.

The dissociative excitation reaction of BrCN with a microwave (MW) discharge flow of Ar produces CN radicals efficiently [9–16]. When this reaction is applied in the CVD process, a-CN_x films are produced. According to the results of our systematic studies, these films have been found to have the following characteristics. The [N]/([N] + [C]) ratio is as high as 0.5 [17,18]. When the water molecules are removed from the reaction system *and* the radio-frequency (typically 13.56 MHz) bias voltage is applied to the substrate, the hardness of the films can reach as high as that of diamond-like carbon (DLC) films [19,20]. In addition, hydrogenated a-CN_x (a-CN_x:H) films formed in a reaction system including impurity water molecules show excellent properties of field emission [21,22] and hydrogen absorption [23,24].

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The overall process of CVD in the above reaction is considered to be composed of three elementary processes. The first is the decomposition of BrCN to produce radical species. The second is the gas-phase transfer and the reactions of these species. The third is the deposition of the precursor radicals on the film surface. For the first process, we have determined the absolute densities of Ar^+ and $CN(X^2\Sigma^+)$ measured by using the electrostatic-probe method and the LIF spectrum of the $CN(A^2\Pi_i–X^2\Sigma^+)$ transition, respectively [25,26]. In these studies, the precursor of the film formation is the $CN(X^2\Sigma^+)$ radicals; the other species such as C and N atoms are little importance. In addition, they are formed almost uniquely by the decomposition of BrCN via charge transfer from Ar^+ followed by recombination with free electrons

$$Ar^+ + BrCN \rightarrow BrCN^+ + Ar \quad (1)$$

$$BrCN^+ + e^- \rightarrow CN(X^2\Sigma^+) + Br. \quad (2)$$

For the second process, the dominant loss process of $CN(X^2\Sigma^+)$ in the gas-phase is the reaction with BrCN [26]:

$$CN(X^2\Sigma^+) + BrCN \rightarrow Br + C_2N_2. \quad (3)$$

For the third process, we have proposed the methodology to determine the sticking probability, s, of $CN(X^2\Sigma^+)$ radicals onto the a-CN_x:H film based on the measurement of the $CN(X^2\Sigma^+)$ radical density, $n_{CN(X)}$, from the intensity calibration of the $CN(A^2\Pi_i–X^2\Sigma^+)$ LIF spectrum [27,28]. It is found, however, that the procedure of the analysis of the LIF spectra employed in Refs. [27,28] includes a problem as pointed out in Ref. [26] and the estimation of error of s is inadequate. The present study reports on a further refinement of the determination of s.

The principle of the determination of s is as follows. Generally, s is defined as the fraction of the flux of the precursor radicals that are chemisorbed onto the film [1]. The flux of the $CN(X^2\Sigma^+)$ radicals arriving at the substrate can be evaluated as $n_{CN(X)}V$, where V is the speed of $CN(X^2\Sigma^+)$. The flux of $CN(X^2\Sigma^+)$ incorporated into the film can be evaluated as $N_{a\text{-}CN}/At_d$, where $N_{a\text{-}CN}$ is the number of CN molecules in the film, A the area of the substrate, and t_d is the deposition time. Then, s can be evaluated as

$$s = N_{a\text{-}CN}/n_{CN(X)}VAt_d. \quad (4)$$

The $n_{CN(X)}$ value can be measured, as in our previous study [26], from the LIF spectroscopy of the 4–0, 5–1, and 7–2 bands of the $A^2\Pi_i–X^2\Sigma^+$ transition, whose intensity is calibrated against the effective lifetime of the $CN(A^2\Pi_i)$ state, laser energy, spatial profile of the laser-beam, and the Rayleigh-scattering intensity of Ar with its cross-section being known [29]. In the flowing-afterglow system like in this study, V can be assumed to be equal to the flow speed. $N_{a\text{-}CN}$ can be evaluated from the weight of the film deposited under the assumption that the [N]/([N] + [C]) ratio of the film is 0.5 [27,28]. Therefore, the present methodology of determining s is rather simple.

In the reported papers on the direct determination of the sticking probability of free radicals [30–32], a complicated procedure of analysis has been used, and the probability thus obtained has, in general, a large uncertainty. Such complication and uncertainty are presumably due to the low efficiency of the film production and to the usage of the mass spectrometric detection of the precursor radicals where the calibration procedure to obtain absolute radical density includes inevitable ambiguity. The present study utilizes the special reaction producing selectively and efficiently the precursor CN radicals having strong transition in the visible-wavelength region. Therefore, the a-CN_x films can be formed with high deposition rate, and simultaneously, the LIF spectroscopy is applicable to determine $n_{CN(X)}$. With aided by these specialties, the present study demonstrates the potential of the LIF spectroscopy to analyze the deposition process of free radicals in the thin-film processing by plasma.

2. Experimental

2.1. MWCVD apparatus

Fig. 1 shows a schematic diagram of the MWCVD apparatus used in the present study. It consists of a stainless-steel chamber with the outer diameter of 101.6 mm and a Pyrex glass tubing system with outer diameters of 15–25 mm which are evacuated by a combination of mechanical-booster (110 m^3/h) and oil-rotary (670 l/min) pumps. Ar was excited by a microwave (MW) discharge (2.45 GHz, 60 W). The pressure of Ar, P_{Ar}, in the chamber was in the range of 0.40–0.70 Torr. Just under the discharge section, a trace amount of BrCN was introduced through a stainless-steel nozzle with the inner diameter of 1 mm to produce the CN radicals. The CN radicals formed in the glass tubing system were effused into the chamber, and were excited by a dye-laser beam from the $X^2\Sigma^+$ state to the $A^2\Pi_i$ state. The distance between the nozzle tip and the laser beam was ≈0.5 m. The inner wall of the chamber was coated with Aquadag (Acheson). The $A^2\Pi_i–X^2\Sigma^+$ LIF signal generated at a right angle to the dye-laser beam was monitored through three lenses (L_1, L_2, and L_3), a slit (S), and a photomultiplier tube (PMT) (Hamamatsu R955). The width and height of S were set to be 10 and 1 mm, respectively; the image of S at the center of the chamber was

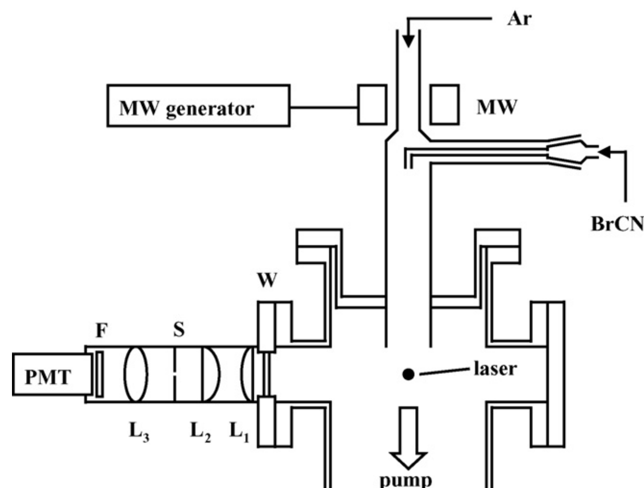

Fig. 1. MWCVD apparatus used in the present study.

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