Carbon system syntheses on a chip by multiple microplasma CVD

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Abstract

Different carbon nitride films are deposited in this study using a multiple DC microplasma chemical vapor deposition apparatus, a so-called plasma chip. Numerical evidence is obtained for the high deposition rate. It probably results from the high density of microplasma demonstrated with a simulation of DC microplasma by the particle-in-cell-Monte Carlo collision method. Moreover, we propose an RF apparatus with a carbon film matrix for improvement of disposability of electrodes of the DC apparatus.

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1. Introduction

Recently, microplasma has attracted much interest. Many studies have addressed the generation of microplasma, including microplasma generation with the scanning probe microscope technique [1], generation of microhollow cathode discharges [2], miniaturized inductively coupled plasma generation [3], microplasma generation with coplanar film electrodes (CFE) [4,5], and thermoelectron-enhanced microplasma generation [6].

From the viewpoint of material development, microplasma shows great promise because of its advantages. It has high density and is capable of being generated in a small space; it can also be obtained at low cost. For example, many high-density microplasmas can be generated in a small space simultaneously using a plasma chip [7,8]. Moreover, samples can be fabricated at a high deposition rate, which can be an advantage for material development. To date, we have confirmed the high density of the DC H2 microplasma generated with CFE by optical emission spectroscopy (OES) [7]. In addition, carbon films were deposited with a prototype plasma chip [8].

This study presents carbon system syntheses on a chip by multiple microplasma chemical vapor deposition (CVD) using DC and RF apparatuses. First, different carbon nitride films are deposited using the multiple DC microplasma CVD apparatus. The high deposition rate was confirmed quantitatively. The high density of microplasma was confirmed by a computational method with ‘NEPTUNE’ software [9], which uses the particle-in-cell-Monte Carlo collision (MCC) method [10,11], for a 10-μm-gap DC H2 plasma previously observed by OES [7]. In addition to various plasma diagnostics, computational simulation methods might be useful for examining microplasma characteristics because experimental analyses of microplasma are difficult to perform because of its small scale. Next, because the electrodes were in a disposable state for only 2–3 min because of damage from the plasma for DC, an array of RF microplasmas and applying these RF plasmas for simultaneous processing with the same concept as a plasma chip were demonstrated.

2. Experimental

2.1. Multiple DC microplasma CVD: plasma chip

2.1.1. Carbon nitride film deposition

Carbon nitride films were deposited with a CH4:N2 gas system using a prototype plasma chip (Fig. 1) with 2 × 3 pairs of electrodes. Plasma was generated with DC power and 20-μm-gap platinum CFE. Gaseous ratios of N2:CH4 used were 5:1, 3:1 and 1:1. Total pressure was 600 Torr. The electric current was controlled at 1.0, 1.5, 2.0 and 2.5 μA.
of one step. This process is repeated until an equilibrium state is reached.

Table 2 lists calculation conditions, such as voltage and environmental pressure, depending on those previously reported [7]. Here, we calculated the microplasma generated with a DC bias voltage of 350 V in H2 gas of 760 Torr pressure with electrodes 10 μm apart. The calculated field was $2 \times 11 \text{m}^2$, which was separated to $4 \times 22$ by a grid for field solving. The upper and bottom boundaries without electrodes were simulated as periodic boundaries. The electrodes were located 10 μm apart and 0.5 μm from the left and right edges. The secondary emission coefficient (γ) on the cathode was set at 0.19 for an ion whose kinetic energy was more than 4.72 eV, which is one of the reported work functions for platinum. One superparticle was given the weight of $10^{15} \text{cm}^{-3}$.

For H2 plasma simulation, 14 reactions were considered. Table 3 shows those reactions, which include those of elastics, various excitations, ionizations, and charge exchange. Cross-sections for the MCC method were obtained from the literature [12,13]. A two-step ionization mechanism was not considered in these reactions. For ionization, only H$_2^+$ and H$^+$ ions created by electronic collisions with H$_2$ molecules were considered. The H$_2^+$ ionic transport was controlled by symmetric charge exchanges H$_2^+$/H$_2$. No reactions with H$^+$ were confirmed because the H$^+$ density was 1.5 orders lower than the H$_2^+$ density in our calculation. Therefore, in this simulation, calculations for electrons and H$_2^+$ ions were considered to be the most important and might be meaningful. Additionally, calculation results obtained from these reactions for macroscale plasma concurred well with previously reported results.
calculated for electrons and $H_2^+$ ions. They were comparable to experimental results [14].

2.2. Development of multiple RF microplasma CVD apparatus

Fig. 2(a) shows a schematic diagram of the generators. It shows capacitive coupled-type plasma (CCP) generators arrayed to the $y$ direction, which has different torch–sample distances ($z$ direction), and a substrate that can be moved to the $x$ direction. Glass tubes with 1 mm outer diameter and 0.5 mm inner diameter were used for tubes of torches; 100 $\mu$m diameter tungsten wires were used for inner electrodes. Torches and substrate were located in a plastic chamber. An RF power source (450 MHz, 30 W) was employed for simultaneous generations.

Carbon films were deposited on a nickel substrate using this apparatus with a CH$_4$ and Ar gas system. Environmental pressure was 760 Torr. The eight torch–substrate distances were slightly changed from 0.7 to 1.2 mm. The gaseous ratio of Ar to CH$_4$ was changed from 500:0.8 to 500:3.0. The total Ar flow rate was fixed at 500 ml/min. Respective deposition times were 3 min.

3. Results and discussion

3.1. Multiple DC microplasma CVD: plasma chip

3.1.1. Carbon nitride film deposition

Films deposited on the cathodes were characterized by FT-IR measurements as carbon nitride films. The films were amorphous, but the N content increased concomitant with increase in the gaseous ratio of N$_2$:CH$_4$. That change was detected by the change in the peak intensity ratio of N–H at around 3330 cm$^{-1}$ to C–H at around 2950 cm$^{-1}$. Respective results and gas ratios for 1.5 $\mu$A were: 1.0 for 1:1 (N$_2$:CH$_4$), 2.5 for 3:1, and 2.8 for 5:1 (Fig. 3). Surface tracer measurements indicated the thickness distribution of the deposited films. As a typical example, the morphology for N$_2$:CH$_4 = 3:1$ with an electric current of 2.5 $\mu$A and a deposition time of 60 s (Fig. 4) indicates that the maximum thickness is 30–40 $\mu$m away from the gap, which was estimated to be 1.02 $\mu$m. Moreover, the films deposited on the anode and the damaged electrodes were confirmed. The maximum deposition rate increased with increased current, such as in the cases of the gaseous ratio of N$_2$:CH$_4 = 3:1$: 0.39 $\mu$m/min for 1.0 $\mu$A, 0.60 $\mu$m/min for 1.5 $\mu$A, 0.75 $\mu$m/min for 2.0 $\mu$A, and 1.02 $\mu$m/min for 2.5 $\mu$A.

Figs. 5(a) and (b) show surface morphology of the film shown in Fig. 4 around the region with maximum film thickness (circle a in Fig. 4) and that of the platinum cathode used as the substrate. These images show that the film was deposited. The grain size was estimated to be about 0.2–0.5 $\mu$m with roughness of about 14 nm as a root mean square.

3.1.2. Simulation of DC microplasma by PIC-MCC method

Figs. 6 and 7 show calculated distributions of potential and the electron density between the electrodes (only the region between the electrodes is shown for simplicity). From these distributions, the bulk, 1.5 $\mu$m thick, located near the anode and the thickness of the cathode sheath, about 8 $\mu$m, are relatively large. They combine to more than one-half of the gap distance. The anode sheath is estimated to be about 0.5 $\mu$m thick. This structure agrees well with experimental observation by optical microscope. Figs. 8 and 9 show distributions of electron and H$_2^+$ ion energies, respectively. Fig. 8 shows electrons are accelerated (up to about $10^5$ eV) in the cathode sheath; they

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**Fig. 2.** Schematic diagram of multiple RF microplasma generators.

**Fig. 3.** Results of FT-IR measurements for the electric current of 1.5 $\mu$A.
yield excitation and ionization. Electron density, electron energy, and H$_2^+$ ion energy in the bulk (the region 0.5–2.0 $\mu$m away from the anode) are approximately 2.5–6.0 $\times$ 10$^{21}$ m$^{-3}$, 0.3–3.0, and 0.06–0.20 eV, respectively. In addition, the electron density agrees with the reported value that was estimated using OES [7]. With an electron density of 5.5 $\times$ 10$^{21}$ m$^{-3}$ and an electron energy of 0.4 eV (with H$_2^+$ ion energy of 0.065 eV) at the center of the plasma, the Debye length $\lambda_D$ is estimated to be ca. 0.065 $\mu$m, which is much smaller than the length of the plasma region ($L$), 1.5 $\mu$m. Also, the ion energy was found to be much lower than the electron energy. Therefore, this plasma is a high-density nonequilibrium plasma with a relatively large cathode sheath. Such high microplasma density, not only for this H$_2$ microplasma, might result from the highly dense (760 Torr) environment because the ionization coefficient is about 10$^{-4}$. That value is on the same order as the conventional macroscale.

3.2. Development of multiple RF microplasma CVD apparatus

Eight CCPs were generated simultaneously, as shown in Fig. 10. The plasma was very stable, with a duration time greater than one hour. That time is much longer than the duration time of DC microplasma with CFE of a few
minutes [5]. Moreover, this apparatus is not disposable: many experimental series can be performed by changing substrates. Fig. 11 shows one example of a nickel substrate after a series of six processing cycles. Energy dispersive spectrometer measurements indicate that the deposited films (shown as circle shapes) are carbon films. No marked structural differences have been identified between the films, depending on deposition conditions of torch–substrate distances and gaseous ratios. However, we obtained a matrix of samples on one chip (substrate) with very stable RF microplasmas.

4. Conclusions

Different carbon nitride films were deposited successfully at a high deposition rate using a prototype plasma chip. It was confirmed quantitatively to be about 1 μm/min in the maximum case in this study. We inferred that the high deposition rate results from the high microplasma density. Characterization by computer simulation using the PIC-MCC method was performed for microplasma that was generated with a DC bias voltage of 350 V in H$_2$ gas of 760 Torr pressure with electrodes 10 μm apart. These results demonstrate that the plasma generated is a nonequilibrium high-density plasma with an electron density higher than 10$^{21}$ m$^{-3}$. Results were confirmed experimentally and computationally. The cathode sheath is relatively thick. Moreover, a multiple RF microplasma CVD apparatus was developed: it improves duration time while providing multiple stable operations. Its high processing rate and possible simultaneous processing lead us to anticipate successful development of numerous materials with these microplasma CVD devices. Processing by these devices will engender deeper understanding through simulation methods: they will become an effective means for elucidating microplasma details.

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Fig. 8. Distributions of electron energy (10 μm gap, H$_2$ 760 Torr, 350 V). (a) x = 0–10 μm, (b) x = 8–10 μm.

Fig. 9. Distributions of H$_2^+$ ion energy (10 μm gap, H$_2$ 760 Torr, 350 V). (a) x = 0–10 μm, (b) x = 8–10 μm.

Fig. 10. Simultaneous generation of RF microplasmas.

Fig. 11. Nickel substrate after depositions with total Ar flow of 500 ml/min and total CH$_4$ flows (from left-hand side) of 0.8, 1.1, 1.5, 1.9, 2.2 and 3.0 ml/min.
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