

Effects of Ethylene/Nitrogen Mixtures on Thermal Chemical Vapor Deposition Rates and Microstructures of Carbon Films

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When ethylene/nitrogen (C_2H_4/N_2) mixtures are used to deposit carbon films by thermal chemical vapor deposition (CVD), effects of $C_2H_4/(C_2H_4 + N_2)$ ratios on the deposition rate and microstructures of carbon films are investigated. Experimental results reveal that the deposition rate of carbon films increases with the $C_2H_4/(C_2H_4 + N_2)$ ratio, and also, raises with the residence time, deposition temperature, and working pressure. The kinetics of this thermal CVD process is discussed. The deposition rate of carbon films is proportional to the $C_2H_4/(C_2H_4 + N_2)$ ratio with a power of second order, which is resulted from the adsorption of remaining precursor gases C_2H_4 on the silica glass plate substrate. Few nitrogen and hydrogen atoms are incorporated into carbon films. As the partial pressure of C_2H_4 is smaller than a threshold pressure or the residence time is shorter than a threshold residence time, no film is related to the activation energy of C_2H_4 dissociation. The degree of ordering and nano-crystallite size of carbon films decrease with increasing the $C_2H_4/(C_2H_4 + N_2)$ ratio, while the sp^3 carbon atoms of carbon films increase. Finally, the results of thermal CVD carbon deposition using C_2H_4 are compared with those using methane and acetylene.

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Because carbon possesses many allotropes with different bonding types and structures, carbon films have many excellent properties including wide bandgap, infrared transparency, high hardness, inertness to chemical attack, and high water resistance.^{1,2} One kind of carbon films called pyrolytic carbon films can be formed by decomposing hydrocarbons in a heating reactor using thermal chemical vapor deposition (CVD), and they were employed as hermetic optical fiber coatings³ or graphite anodes of lithium ion secondary batteries.^{4,5} When carbon films are prepared by thermal CVD, their properties are affected by many factors such as the precursor gas, deposition temperature, working pressure, and mass flow rate of inlet gas.³⁻⁶ Among the precursor gases, methane (CH_4) remains a popular choice because it is available in high purity, but its growth rate is lower.¹ Alternatively, acetylene (C_2H_2) is a very useful source gas for low pressure deposition, because its strong $C \equiv C$ bond means it has a simple dissociation pattern, giving mainly $C_2H_n^+$ ions.⁷ Nevertheless, the degree of ordering of carbon films using C_2H_2 is lower, and the outlet of thermal CVD system are covered with contaminants including asphalts.

Ethylene (C_2H_4) is an important product of petrochemical industry, so it is also often chosen as the precursor gas to prepare carbon films using different methods such as ion beam deposition,⁸ microwave surface-wave plasma CVD,9,10 electron beam induced deposition,11 and dielectric barrier discharge plasma.¹² Recently, we have adopted CH_4 and C_2H_2 as the precursor gas to study the properties of thermal CVD carbon films.^{13,14} However, we have found no evidence of previous works to investigate the effects of C_2H_4 on the properties of carbon films using thermal CVD in detail. Hence, this study will investigate the effect of $C_2H_4/(C_2H_4 + N_2)$ ratios on the thermal CVD deposition rate and microstructures of carbon films on silica glass plates. At a certain $C_2H_4/(C_2H_4 + N_2)$ ratio, the effects of the mass flow rate of inlet gases, deposition temperature, and working pressure on the deposition rate will be also considered. Furthermore, the kinetics of the thermal CVD process using C_2H_4/N_2 mixtures will be discussed, and the connection between the thermal CVD process and microstructure of carbon films will be also considered. Finally, the thermal CVD carbon deposition using C_2H_4 is compared with those using CH_4 and C_2H_2 .

Experimental

Preparation of carbon films.— The preparation of carbon films proceeded as follows. The silica glass plate (length = 12 mm, width

= 12 mm, height = 1 mm) were cleaned in ultrasonic baths of acetone and de-ionized water, in that order, to improve the adhesion of carbon films onto these substrates. Then, the silica glass plates were coated with carbon films by thermal CVD. The thermal CVD system adopted a quartz tube as the reaction chamber, which had a length of 900 mm, an internal diameter of 25 mm, and a wall thickness of 1.5 mm. The deposition zone length of the reaction chamber was 60 mm, and the substrate was placed in the reaction chamber so that the middle portion of the substrate's length coincides with that of the deposition zone. 99.9% C_2H_4 and 99.995% N_2 were used as the precursor gases. The mass flow rates of $(C_2H_4 + N_2)$ were kept at 40 sccm (standard cubic centimeter per minute, cm³/min), and five carbon films were prepared with the $C_2H_4/(C_2H_4 + N_2)$ ratios of 60, 70, 80, 90, and 100%. The working pressure was maintained at 60 ± 2 kPa by a mechanical pump. The temperature rose from room temperature to deposition temperature at a rate of 15 K/min. The deposition temperature and deposition time were set to 1033 ± 1 K and 30 min, respectively. During the deposition process, a residual gas analyzer (RGA, BCTECH-XT200M) was used to measure the partial pressures of the residual gases. After the deposition process was finished, the temperature was quickly reduced to room temperature at a rate of 250 K/min by cooling in air with a fan.

In thermal CVD process, the deposition rate depends on not only the gas phase composition $C_2H_4/(C_2H_4 + N_2)$ but also the mass flow rate (or residence time) of inlet gases, deposition temperature, and working pressure. To understand the effect of the mass flow rate of inlet gases, deposition temperature, and working pressure on the deposition rate, other kinds of carbon films were prepared. In those cases, the $C_2H_4/(C_2H_4 + N_2)$ ratio, mass flow rate of $(C_2H_4 + N_2)$, deposition temperature, working pressure, and deposition time were set to 80%, 40 sccm, 1033 K, 60 kPa, and 30 min, respectively, with the exception of the specified parameters.

Characterization of carbon films.— The thicknesses and morphologies of the carbon films were obtained by measuring the cross sections of the silica glass plates located at the middle portion of the length using a field emission scanning electron microscope (FE-SEM, JEOL JSM-6700F). The operating voltage of the FESEM was 3 kV. The microstructure of carbon films was investigated by high-resolution X-ray diffraction meter (HRXRD, Brukers D8 Discover), Raman scattering spectrometer (RSS, Jobin Yvon Triax 550), and X-ray photoelectron spectroscopy (XPS, ULVAC-PHI PHI 5000 VersaProbe). All the measurements of microstructures were made on the carbon films located at the middle portion of the substrate.

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Figure 1. FESEM images of cross sections of carbon films deposited at different $C_2H_4/(C_2H_4 + N_2)$ ratios.

HRXRD was performed using $Cu K_{\alpha}$ radiation ($\lambda = 0.154$ nm) with an incident angle of 0.15 degrees. Diffraction peaks from the carbon films were discerned by 2 θ angles ranging between 10 and 50 degrees. Data from the Joint Committee on Powder Diffraction File (JCPDF) database (Number: 75-1621) were used to identify the microstructure of the carbon films from the diffraction peaks. RSS was measured in back-scattering geometry with the 633 nm line of a He-Ne laser at room temperature in the spectral range of 1000–2000 cm⁻¹. Alternatively, XPS used $Mg K_{\alpha}$ radiation (Photo energy = 1253.6 eV) as an excitation source was utilized to measure the binding energy spectra of carbon films. All carbon core lines (*C1s*) spectra were acquired when the X-ray incident angle was 54° to enhance the contribution of carbon films on this core line shape.

Deposition Rate

Effects of $C_2H_4/(C_2H_4 + N_2)$ ratios.— Figure 1 shows FESEM images of cross sections of carbon films that are deposited on silica glass plates with different $C_2H_4/(C_2H_4 + N_2)$ ratios. The thicknesses t_f of carbon films are obtained by measuring cross sections of the silica glass plates located at the middle portion of the length. Experimental results show that the thicknesses of carbon films are 133, 191, 259, 383, and 417 nm for the $C_2H_4/(C_2H_4 + N_2)$ ratio being 60, 70, 80, 90, and 100%, respectively. Notably, the carbon film was uniformly deposited on the silica glass plate, and the error in the film thickness was within 5%. After the thicknesses of the carbon films are obtained using an FESEM, the deposition rate r_f of the carbon films can be calculated from the film thickness and deposition time. Figure 2a shows that the deposition rate r_f of carbon films on silica glass plates are 4.4, 6.4, 8.6, 12.8, and 13.9 nm/min for the $C_2H_4/(C_2H_4 + N_2)$ ratio being 60, 70, 80, 90, and 100%, respectively. This indicates that the deposition rate of carbon films increases with increasing the $C_2H_4/(C_2H_4 + N_2)$ ratio. Our experimental result also shows that as the $C_2H_4/(C_2H_4 + N_2)$ is not larger than 6.3%, no films can be formed. Hence, the relation between the deposition rate of carbon films and



Figure 2. (a) The deposition rate of carbon films as a function of the $C_2H_4/(C_2H_4 + N_2)$ ratio, $C_2H_4/(C_2H_4 + Ar)$ ratio, and residence time stayed at the deposition zone. (b) The dependence of the deposition rate of carbon films on the deposition temperature and working pressure.

 $C_2H_4/(C_2H_4 + N_2)$ ratio can be expressed by a power function:

$$r_f = k_1 [C_2 H_4 / (C_2 H_4 + N_2) - 0.063]^n,$$
^[1]

where constants k_1 and n are obtained as 16.7 nm/min and 2.07, respectively.

Effects of total mass flow rates.— To understand the effect of the mass flow rate m on the deposition rate, seven carbon films are prepared with the mass flow rates of $(C_2H_4 + N_2)$ being 20, 40, 60, 80, 100, 120, and 160 sccm. In this case, the other unspecified process parameters are kept the same as those described in the experimental section. Table I shows that the deposition rates are 48.2, 8.6, 2.8, 2.1, 1.1, 1.0, and 0.3 nm/min for the mass flow rates of $(C_2H_4 + N_2)$ being 20, 40, 60, 80, 100, 120, and 160 sccm, respectively. This indicates that the deposition rates decrease with increasing the mass flow rates of $(C_2H_4 + N_2)$. The mass flow rate of $(C_2H_4 + N_2)$ is related to the residence time, τ , of the precursor gas stayed in the deposition zone. Although the precursor gas is decomposed in the deposition zone, the relation between the mass flow rate and residence time can be approximately estimated as follows. Based on the conservation of volume, the average flow velocity, v_{av} , of the precursor gas in the deposition zone can be obtained as $v_{av} = V/(\pi d^2/4 - t \times w)$. Here V, d = 25 mm, t = 1 mm, and w = 12 mm are the volume flow rate, the internal diameter of the reaction chamber, the thickness of the silica glass plate, and the width of the silica glass plate, respectively. Moreover, the volume flow rate \mathbf{V} can be approximately obtained from

Table I. The film thickness t_f , deposition rate r_f , average flow velocity v_{av} , and residence time τ at various mass flow rates of $(C_2H_4 + N_2)$.

Mass flow rate of $(C_2H_4 + N_2)$ (sccm)	20	40	60	80	100	120	160
t_f (nm)	1446	258	84	63	33	30	10
r_f (nm/min)	48.2	8.6	2.8	2.1	1.1	1.0	0.3
v_{av} (mm/s)	4.43	8.85	13.3	17.7	22.1	26.6	35.4
τ (s)	6.8	3.4	2.3	1.7	1.4	1.1	0.85

the ideal gas equation as: $V = \frac{n}{RT}/p$. In this study, the working pressure p is 60 kPa; the gas constant R is 8.31 J/K \cdot mole; the deposition temperature T is 1033 K, and $n \text{ (mole/min)} = m \text{ (sccm)} \times 4.46$ $\times 10^{-5}$ (mole/cm³). Table I indicates that the average flow velocities, v_{av}, are 4.43, 8.85, 13.3, 17.7, 22.1, 26.6, and 35.4 mm/s for mass flow rates of $(C_2H_4 + N_2)$ being 20, 40, 60, 80, 100, 120, and 160 sccm, respectively. On the other hand, the length L of the deposition zone is 60 mm and the thickness of the carbon film was measured at the place located at the middle of the deposition zone, and thus, the residence time, $\boldsymbol{\tau},$ of the precursor gas stayed in the deposition zone can be obtained as: $\tau = L/(2v_{av})$. Table I also show that the residence times τ are 6.8, 3.4, 2.3, 1.7, 1.4, 1.1, and 0.85 s for the mass flow rates of $(C_2H_4 + N_2)$ being 20, 40, 60, 80, 100, 120, and 160 sccm, respectively. Figure 2a plots the relation between the deposition rate and residence time, indicating that the deposition rate exponentially increases with increasing the residence time. Notably, our experimental result also shows that if the mass flow rate of $(C_2H_4 + N_2)$ is larger than 200 sccm (that is, the residence time is smaller than 0.68 s), no film can be formed. Hence, the dependence of the deposition rate on the residence time can be represented as

$$r_f = k_2[\exp(q\tau) - \exp(q\tau_c)], \qquad [2]$$

where τ_c (= 0.68 s) is the threshold residence time, and constants k_2 and q are obtained as 2.69 nm/min and 0.44/s, respectively, with an error within 10%.

Effects of deposition temperatures.— To understand the effect of the deposition temperature *T* on the deposition rate, five carbon films were prepared with the deposition temperatures of 1013, 1023, 1033, 1043, and 1053 K. In this case, the other unspecified process parameters are kept the same as those described in the experimental details. Figure 2b shows that if the deposition rates are 2.2, 4.2, 8.6, 11.6, and 21.0 nm/min, respectively. This indicates that the dependence of the deposition rate on the deposition temperature follows the Arrhenius law. Hence, the constant k_1 in Eq. 1 can be replaced by

$$k_1 = k_0 \exp(-E/RT), \qquad [3]$$

where E (= 448 kJ/mole) is the activation energy with a derivation within 10%; R (= 8.31 J/K · mole) is the gas constant, and k_0 = 6.13 × 10²³ nm/min. Notably, as the temperature changes from 1013 to 1053 K, the residence time varies from 3.47 to 3.35 s. Because the variation of the residence time is small, we assume that the residence time is not changed here.

Effects of working pressures.— To further understand the effect of the working pressure on the deposition rate, seven carbon films were prepared with the working pressures of 23, 33, 40, 47, 53, 60, and 67 kPa, where the derivation of working pressures is within 2 kPa. In this case, the other unspecified process parameters are kept the same as those described in the experimental details. Figure 2b reveals that if the working pressures are 23, 33, 40, 47, 53, 60, and 67 kPa, the deposition rates are 0.3, 0.6, 1.1, 1.9, 4.5, 8.6, and 14.2 nm/min, respectively. Our experimental result also shows that if the working pressure *p* is not over 12 kPa, no film is formed. Notably, when the



Figure 3. XRD patterns of carbon films deposited at different $C_2H_4/(C_2H_4 + N_2)$ ratios. This figure reveals that XRD patterns include a (002) diffraction peak of graphite and a (220) diffraction peak of silica glass.

working pressure changes from 12 to 67 kPa, the residence time varies from 0 to 3.8 s. Therefore, the dependence of the deposition rate r_f on the working pressure p can be represented as

$$r_f = k_3 [\exp(q\tau) - \exp(q\tau_c)] [(p - p_c)/(p_0 - p_c)]^a, \qquad [4]$$

where p_0 (= 60 kPa) is the reference working pressure; p_c (= 12 kPa) is the threshold working pressure, and k_3 and a are constants to be determined. As stated in section 3.2, the residence time τ in Eq. 4 is related to the working pressure p, and q (= 0.44/s) and τ_c (= 0.68 s) are constants. When the data of the deposition rates at various working pressures are substituted into Eq. 4, the constants k_3 and a are found to be 2.66 nm/min and 2.19, respectively, with an error well below 10%. The amount of C_2H_4 in the reaction gas not only is related to the $C_2H_4/(C_2H_4 + N_2)$ ratio but also is proportional to the working pressure, and thus, the constant a is close to n in Eq. 1. Eqs. 1 and 4 show that the deposition rate is proportional to the partial pressure (or pressure) of C_2H_4 with a power of second order, and thus, the thermal CVD process of this work is a second-order reaction.

Structural Analyzes

Figure 3 shows HRXRD patterns of carbon films that are prepared with different $C_2H_4/(C_2H_4 + N_2)$ ratios. This figure displays a (220) diffraction peak around 20.8 degree for the silica glass substrate and a (002) diffraction peak around 25.5 degree for the graphite, and thus, the (220) peak of the silica glass substrate should be extracted from the HRXRD pattern to obtain the (002) peak of the graphite. Moreover, to eliminate the intrinsic instrumental broadening, the B parameter was calculated using the equation, $B = (B_c^2 - B_{Si}^2)^{1/2}$, where B_c is the full-width-at-half-maximum (FWHM) of the (002) peak of the carbon films, and B_{Si} is the experimentally obtained FWHM of the (220) peak of a standard silicon sample.¹⁵ Because the thickness of the carbon film with the $C_2H_4/(C_2H_4 + N_2)$ ratio of 60% is relatively small (= 133 nm), the (220) diffraction peak of the silica glass substrate is larger than the (002) diffraction peak of graphite. Hence, the fitting result of (002) diffraction peak of graphite with the $C_2H_4/(C_2H_4)$ $+ N_2$) ratio of 60% has less accuracy. Experimental results reveal that the diffraction angle of the (002) peak of the graphite decreases from 25.4 to 25.2 degrees as the $C_2H_4/(C_2H_4 + N_2)$ ratio increases from 70 to 100%, while B parameter of carbon films increases from 4.5 to 5.7 degrees. These results indicate that the degree of ordering of carbon films decreases with increasing the $C_2H_4/(C_2H_4 + N_2)$ ratio.⁵ The mean crystallite size, L_c , of carbon films can be estimated



Figure 4. (a) Raman spectra of carbon films deposited at different $C_2H_4/(C_2H_4 + N_2)$ or $C_2H_4/(C_2H_4 + Ar)$ ratios. The Raman spectra contain the *D* band at about 1350 cm⁻¹, *G* band at about 1580 cm⁻¹, *D'* band at about 1620 cm⁻¹, *D* band at about 1200 cm⁻¹, and *D* band at about 1500 cm⁻¹. (b) Fitting results of Raman spectra for carbon films deposited at different $C_2H_4/(C_2H_4 + N_2)$ or $C_2H_4/(C_2H_4 + Ar)$ ratios.

using Scherrer's formula, $L_c = 0.9\lambda/(B\cos\theta_B)$. Here λ (= 0.154 nm) is the wavelength of the copper K_{α} X-ray line; *B* is the *FWHM* of an HRXRD peak, and θ_B is the diffraction angle of the HRXRD peak.¹⁶ The calculated result shows that the mean crystallite size (L_c) of carbon films decreases from 2.0 to 1.5 nm as the $C_2H_4/(C_2H_4 + N_2)$ ratio increases from 70 to 100%. The decrease of the mean crystallite size (L_c) of carbon films indicates that the degree of ordering of carbon films decreases. This also implies that the increase of the $C_2H_4/(C_2H_4 + N_2)$ ratio raises the deposition rate of carbon films, but decreases the degree of ordering of carbon films.

Figure 4a shows Raman spectra (RS) of carbon films that are prepared with different $C_2H_4/(C_2H_4 + N_2)$ ratios. The RS can be de-

composed into five absorption peaks: D band at about 1350 cm^{-1} G band at about 1580 cm⁻¹, D' band at about 1620 cm⁻¹, D1 band at about 1200 cm⁻¹, and D2 band at about 1500 cm⁻¹, where the D, G, D', and D1 bands were fitted with Lorentzian function, and the D2 band was fitted with Gaussian function.¹⁷ The D band is associated with the breathing mode of sixfold sp^2 rings and identified as the disorder-activated band, this mode is forbidden in perfect graphite and only becomes active in the presence of disorder;¹⁸ the *G* band is associated with the bond stretching vibrations of all sp^2 sites;¹⁸ the *D'* band is related to disordered graphitic lattice;¹⁷ the D1 band is also related to the disorder graphitic lattice¹⁷ but not uniquely defined,¹⁹ and the D2 band is attributed to amorphous carbon.¹⁷ Figure 4b shows the peak shift of the D band (ω_D) and G band (ω_G) , the full-width-at-halfmaximum of D band ($FWHM_D$) and G band ($FWHM_G$), and integrated intensity ratio of the D band to G band (I_D/I_G) for carbon films prepared with different $C_2H_4/(C_2H_4 + N_2)$ ratios. This figure shows that as the $C_2H_4/(C_2H_4 + N_2)$ ratio increases, ω_D and ω_G have no apparent trend. Alternatively, this figure also reveals that as the $C_2H_4/(C_2H_4)$ $+N_2$) ratio increases from 60 to 100%, FWHM_D increases from 154 to 162 cm^{-1} and I_D/I_G values increase from 2.90 to 3.28, while FWHM_G values decrease from 54 to 50 cm⁻¹. This indicates that the degree of ordering of carbon films decreases with increasing the $C_2H_4/(C_2H_4)$ $+ N_2$) ratio.¹⁸ The ratio of I_D and I_G is commonly used to approximately estimate the crystallite size of nanographite. An expression that gives the crystallite size (L_a) from the integrated intensity ratio I_D/I_G is given by:¹⁵ $L_a(nm) = (2.4 \times 10^{-10})\lambda_a^4(I_D/I_G)^{-1}$, where λ_o (= 633 nm) is the laser line wavelength used in the Raman experiment. This expression indicates that the crystallite size of nanographite increases with decreasing the I_D/I_G value. Hence, Fig. 4b shows that I_D/I_G increases from 2.90 to 3.28 as the $C_2H_4/(C_2H_4 + N_2)$ ratio increases from 60 to 100%, while L_a decreases from 13.3 to 11.7 nm. The decrease of the crystallite size (L_a) of carbon films also indicates that the degree of ordering of carbon films decreases. This result is consistent with that of XRD.

On the other hand, XPS is adopted to investigate the chemical bonding of carbon films. Figure 5a shows XPS patterns of carbon films that are prepared with different $C_2H_4/(C_2H_4 + N_2)$ ratios. This figure indicates that the C1s core around 285 eV and O1s core around 531 eV are revealed, while the N1s core around 400 eV is not found. This implies that little nitrogen is incorporated into the carbon films. The Ols core shows that oxygen existed in the carbon films. Remarkably, the presence of oxygen is probably related to the incorporation of oxygen due to prolonged exposure of the sample to the external atmosphere before XPS measurements and accidental incorporation during deposition.²⁰ Figure 5b shows C1s patterns of carbon films that are prepared with different $C_2H_4/(C_2H_4 + N_2)$ ratios. The C1s spectra of carbon films can be decomposed into five components: 284.2, 285.0, 286.5, 287.9, and 289.6 eV attributed to sp^2 carbon atoms, sp^3 carbon atoms, C-O bonds, C=O bonds, and COOR, respectively.²¹⁻²³ The C-O bonds, C=O bonds, and COOR are assigned to atomic carbon bonded to surface adsorbents from the ambient, hereafter referred to as satellite peaks.²³ Thus, the sum of the satellite peak areas indicates the fraction of carbon bonding with surface adsorbents. Table II shows the peak position and peak area fraction for all kinds of carbon atoms. This result indicates that the peak positions of sp^2 and sp^3 carbon atoms are slightly changed. Alternatively, if the $C_2H_4/(C_2H_4 + N_2)$ ratio changes from 60 to 100%, the sp^2 peak area fraction decreases from 35.9 to 19.1%, but the sp^3 peak area fraction increases from 35.0 to 51.4%. This implies that if the $C_2H_4/(C_2H_4 + N_2)$ ratio increases, the structure of the carbon films shifts to diamond-like. Table II reveals that the area fraction of satellite peaks is about 30%, which is changed at different $C_2H_4/(C_2H_4 + N_2)$ ratios. This is because the surface of carbon films is exposed to the atmosphere, and the amount of surface adsorbents from the ambient for various carbon films is different.

Discussion

The kinetics of this thermal CVD process is discussed, and the details are described in the Appendix. In brief, the precursor gases



Figure 5. (a) XPS of carbon films deposited at different $C_2H_4/(C_2H_4 + N_2)$ ratios. (b) Decomposed curves of CI_s core for carbon films deposited at different $C_2H_4/(C_2H_4 + N_2)$ ratios.

 $(C_2H_4 \text{ and } N_2)$ are flowed through the reactor and heated up, and thus, some of precursor gases are decomposed. The RGA result (mentioned in the Appendix) reveals that the residual gases in the gas phase mainly contain the remaining precursor gases C_2H_4 (and/or N_2) and the product gases C_2H_2 , C_2H_3 , and H_2 . The deposition rate of carbon films is proportional to the partial pressure of the inlet gas C_2H_4 with a power of second order, and the pyrolysis of C_2H_4/N_2 mixtures is

Table II. The peak positions and peak area fractions of carbon atoms analyzed by XPS at different $C_2H_4/(C_2H_4 + N_2)$ ratios.

$C_2H_4/(C_2H_4 + N_2)$ ratio (%)	60	70	80	90	100
sp^2 peak position (eV)	284.5	284.6	284.4	284.5	284.4
sp^3 peak position (eV)	285.1	285.2	285.2	285.1	285.0
sp^2 fraction (%)	35.9	34.1	26.4	24.1	19.1
sp^3 fraction (%)	35.0	38.7	40.5	45.0	51.4
Satellite fraction (%)	29.1	27.2	33.1	30.9	29.3

resulted from the adsorption of the remaining precursor gases C_2H_4 on the silica glass plate substrate. The carbon species adsorbed on the substrate surface will further diffuse and conjugate to form the laminar graphite structure.

The dissociation energy of N_2 is very high (= 942 kJ/mole),²⁴ and XPS results of this study reveal that little nitrogen is incorporated into the carbon films. Hence, most of N_2 is exhausted to the atmosphere. In other words, the N_2 gas is only used to reduce the partial pressure of C_2H_4 . In the literature, N_2 was often added in the precursor gas to form various kinds of nitrides.²⁵⁻²⁹ Nevertheless, this study reveals that adding N_2 in C_2H_4 is not able to produce nitrides in thermal CVD process. To verify the above statement, an additional experiment was executed as follows. The deposition parameter of this additional experiment is the same as that of various $C_2H_4/(C_2H_4)$ $+ N_2$) ratios with the exception that N_2 is replaced by Ar (99.999%) in purity). Notably, Ar is an inert gas, so it is only used to reduce the partial pressure of C_2H_4 . The deposition rate and RS results of carbon films deposited at various $C_2H_4/(C_2H_4 + Ar)$ ratios are also shown in Figs. 2a and 4b, respectively. Figure 2a reveals that the deposition rate using C_2H_4/Ar mixtures is quite close to that with C_2H_4/N_2 mixtures at the same deposition condition. Alternatively, Fig. 4b also shows that the RS result of carbon films with C_2H_4/Ar mixtures is very similar to that with C_2H_4/N_2 mixtures. Hence, this is evident that the N_2 gas is only used to reduce the partial pressure of C_2H_4 , as the Ar gas does.

The deposition of carbon films on the substrate needs adequate amount of carbon species in the gas phase (or sufficient residence time for carbon species to stay in the deposition zone). Hence, if the partial pressure (or working pressure) of C_2H_4 is smaller than the threshold pressure (or if the residence time is shorter than the threshold residence time), no film can be formed. Moreover, as the residence time of the precursor gas stayed in the deposition zone increases, the amount of decomposed radicals also raises. As RGA results show that C_2H_4 is decomposed to form C_1 and C_2 radicals, and thus, the total amount of C_1 and C_2 species is increasing with the residence time. Consequently, the carbon fragment converted from these decomposed precursor gases to form carbon films on the substrate also exponentially increases.³⁰ The dissociation energy of C_2H_4 was reported as 411 kJ/mole,^{31,32} and thus, the activation energy of 448 kJ/mole in this study is mainly correlated to the dissociation energy of C_2H_4 dissociation.

Figure 1 also illustrates that carbon films exhibit a laminar structure, and there are many particles appeared on the carbon film surface. The pyrolytic carbon films prepared by thermal CVD usually exhibits a laminar structure.³³ The growth of these particles had been studied previously, which proceeded as follows.^{34,35} Initially, a small (nanoscale) particle is nucleated on the carbon film. The laminar carbon film is then deposited around the small particle, extending the shape of the particle to that of a headstand cone with a spherical base. The spherical base of the cone can be evident from the surface of the carbon film. The surface area of this spherical base increases with the carbon film thickness. Additionally, the number of nucleated particles increases with the deposition rate, so the size and number of particles increase as the thickness of the carbon film increases.³⁴ Notably, the degree of ordering of carbon films decreases with increasing the size and number of particles, and thus, XRD and RS results of this study show that the degree of ordering of carbon films decreases with increasing the deposition rate (and also the $C_2H_4/(C_2H_4 + N_2)$ ratio).

Sobol-Antosiak and Ptak³⁶ reported that the degree of surface hydrogen coverage tends to increase in nucleation processes, leading to the formation of carbon films, from gas phase by the CVD methods. The presence of hydrogen is considered to enhance the process of forming films with high sp^3 contribution. In this work, the RGA result shows that the gas phase hydrogen increases as the $C_2H_4/(C_2H_4 + N_2)$ increases. Consequently, the effect of gas phase hydrogen on the formation of carbon films may be taken to explain the reason why the sp^3 fraction in the carbon films increases with increasing the $C_2H_4/(C_2H_4 + N_2)$ ratio.

In our previous works, we adopted CH_4^{13} and $C_2H_2^{14}$ as the precursor gases to study the effect of deposition parameters on the properties

	This work	Reference 13	Reference 13	Reference 14
Precursor gas	C_2H_4 (32 sccm)	<i>CH</i> ₄ (32 sccm)	<i>CH</i> ₄ (32 sccm)	C_2H_2 (32 sccm)
-	N_2 (8 sccm)	N_2 (8 sccm)	N_2 (8 sccm)	N_2 (8 sccm)
Substrate	Silica glass plate	Silica glass fiber	Silica glass plate	Silica glass fiber
Deposition temperature (K)	1033	1248	1248	1003
Working pressure (kPa)	60	77	77	13.3
Deposition rate (nm/min)	8.6	56.7	39.2	5.1
C/H ratio	1/2	1/4	1/4	1/1
Activation energy (kJ/mole)	448	456	Null	484
Power order of controlled process	$2.07\sim 2.19$	$1.15 \sim 1.23$	1.17	4.83
Outlet Contaminants	Moderate	Small	Small	Large

Table III. A comparison between the thermal CVD carbon deposition of this work and that of our previous works^{13,14} at some specified process parameters.

of thermal CVD carbon films. A comparison between the results of this work and those of the previous works^{13,14} at a specified process parameter is listed in Table III. Notably, the specified deposition parameters listed in Table III for various precursor gases are obtained by the authors to form a carbon film with smooth surface and good adhesion on the substrate surface, so they are different. The working pressure in previous work¹⁴ was 13.3 kPa, but it was misprinted as 133 kPa. Table III shows that the deposition temperature of C_2H_4 is smaller than that of CH_4 , but it is slightly larger than that of C_2H_2 . Alternatively, the working pressure of C_2H_4 is slightly smaller than that of CH_4 , but it is larger than that of C_2H_2 . C_2H_4 is a sp^2 hybridized hydrocarbon, while CH_4 and C_2H_2 are sp^3 and sp^1 hybridized hydrocarbons, respectively. Hence, the hydrogen/carbon (H/C) ratio of C_2H_4 is 1/2, while the H/C ratios of CH_4 and C_2H_2 are 1/4 and 1, respectively. The activation energy of C_2H_4 (= 448 kJ/mole) is lower that those of C_2H_2 (= 484 kJ/mole) and CH_4 (= 456 kJ/mole). The pyrolysis of C_2H_4 with added N_2 is controlled by the second-order process to create C_2 species; the pyrolysis of CH_4 with added N_2 is mainly controlled by the first-order process to create C_1 species, and the pyrolysis of C_2H_2 with added N_2 is controlled by the fifth-order process to create C_{10} species. As the process parameters of thermal CVD are kept the same, the deposition rate of CH_4 is much smaller than those of C_2H_4 and C_2H_2 . Alternatively, if the deposition parameters are selected as: deposition temperature T = 1003 K, working pressure p = 13.3 kPa, and mass flow rate of inlet gas m = 40 sccm, our experimental results show that the deposition rates of carbon films on silica glass plate with $C_2H_4/(C_2H_4 + N_2) = 80\%$ and $C_2H_2/(C_2H_2)$ $+ N_2$ = 80% are 0 and 2.6 nm/min, respectively. This means that the deposition rate of thermal CVD carbon deposition using C_2H_4 is smaller than that using C_2H_2 at the same deposition condition. Moreover, it was found that the amount of contaminants in the outlet of thermal CVD system using CH_4 is small; the amount of contaminants in the outlet of thermal CVD system using C_2H_4 is moderate, and the amount of contaminants in the outlet of thermal CVD system using C_2H_2 is large.

Conclusions

When C_2H_4/N_2 mixtures are used to form carbon films by thermal CVD, effects of deposition parameters on the deposition rate and microstructures of carbon films are investigated. Experimental results show that as the $C_2H_4/(C_2H_4 + N_2)$ ratio increases from 60 to 100%, the deposition rate increases from 4.4 to 13.9 nm/min. Alternatively, if the residence time, deposition temperature, and working pressure raise, the deposition rate of carbon films also increases. The deposition rate of carbon films is proportional to the partial pressure of the inlet gas C_2H_4 with a power of second order, and the pyrolysis of C_2H_4/N_2 mixtures is resulted from the adsorption of the remaining precursor gases C_2H_4 on the silica glass plate substrate. Few N and H atoms are incorporated into the carbon films. If the partial pressure (or working pressure) of C_2H_4 is smaller than the threshold pressure or the residence time is shorter than the threshold residence time, no carbon film is formed. The activation energy (= 448 kJ/mole) of carbon deposition is shown to correlate to the activation energy of C_2H_4 dissociation. XRD and RS results show that the degree of ordering and nano-crystallite size of carbon films decrease with increasing the $C_2H_4/(C_2H_4 + N_2)$ ratio, this is because the size and number of particles in the carbon films increase. Alternatively, when the $C_2H_4/(C_2H_4 + N_2)$ ratio increases, the hydrogen in the gas phase also increases, and thus, XPS results reveal that sp^3 carbon atoms in carbon films raise. The results of this work are compared to those using CH_4/N_2 and C_2H_2/N_2 mixtures at a specified process parameter.

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Appendix

The kinetics of this thermal CVD process is described here. In this work, substrates are heated in a deposition reactor and well-mixed precursor gases C2H4 and/or N2 are flowed through the reactor and heated up. After heated up in the deposition reactor, the precursor gas undergoes reactions in the gas phase. Simultaneously, complex heterogeneous reactions occur at the surface of the silica glass substrate. Deposition of the solid-phase carbon materials thus is a consequence of complex homogeneous gas-phase and heterogeneous surface reactions.³¹ The partial pressure of the residual gases in the gas phase was analyzed by residual gas analyzer (RGA). The RGA result reveals that the residual gases contain the remaining precursor gases C_2H_4 and/or N_2 ; the main product gases C_2H_2 , C_2H_3 , and H_2 ; and also, some other secondary product gases CH, CH_2 , CH_3 , CH4, C2, C2H, and C2H5. Notably, the partial pressures of the secondary product gases are much small than those of the excess precursor gases and main product gases, so only the latter gases are considered here. Figure A1 shows the partial pressures, p_i^{out} , of the remaining precursor gases and main product gases as a function of the partial pressure, $p_{C_2H_4}^{in}$, of the inlet gas C_2H_4 . Notably, $p_{C_2H_4}^{in}$ is the multiplication of the $C_2H_4/(C_2H_4 + N_2)$ ratio and 60 kPa. Figure A1 reveals that the partial pressure of the outlet gas C_2H_4 $(p_{C_2H_4}^{out})$ is proportional to $(p_{C_2H_4}^{in})^2$. Alternatively, the RGA result also shows that the partial pressure of the outlet gas C_2H_2 $(p_{C_2H_2}^{out})$ almost equals to that of C_2H_3 $(p_{C_2H_3}^{out})$, which is proportional to $(p_{C_2H_4}^{in})^{0.5}$. The partial pressure of the outlet gas H_2 $(p_{H_2}^{out})$ is also proportional to $(p_{C_2H_4}^{in})^{0.5}$. When the conversion of C_2H_4 into the product gases is a nth-order reaction, the rate equation can be expressed as: $d(p_{C_2H_4}^{in})/dt = -k_n(p_{C_2H_4}^{in})^n$, and thus, one obtains

$$(p_{C_2H_4}^{out})^{1-n} - (p_{C_2H_4}^{in})^{1-n} = k_n(n-1)t_r,$$
[A1]

where k_n is a constant and t_r is the residence time of the precursor gases stayed in the deposition zone. By substituting the data of $p_{C_2H_4}^{uin}$ and $p_{C_2H_4}^{in}$ into Eq. A1, one obtains that n = 0.5. This means that the conversion of C_2H_4 to C_2H_2 (also C_2H_3) is a half-order reaction. Therefore, the partial pressures of the main product gases, $p_{C_2H_2}^{out}$, $p_{C_2H_3}^{out}$, and $p_{H_2}^{out}$, are proportional to $(p_{C_2H_4}^{in})^{0.5}$. Norinaga and Deutschmann³⁷ (also with their coworkers³⁸) had investigated the de-

Norinaga and Deutschmann³⁷ (also with their coworkers³⁸) had investigated the detailed kinetic modeling of gas-phase reactions in the chemical vapor deposition of carbon from light hydrocarbons. Nevertheless, the RGA result of this study shows that the residual gases mainly include C_2H_2 , C_2H_3 , and C_2H_4 species, so only these species will



Figure A1. The partial pressures of the residual gases as a function of the partial pressure of the inlet gas C_2H_4 .

be supposed to be the main species able to adsorb at the deposition surface. Based on Langmuir-Hinshelwood kinetics,^{39,40} we assume that the chemisorption of hydrocarbon species from the gas phase is irreversible, and the surface reactions by ring formation from carbon-hydrocarbon surfaces complexes are fast in comparison to hydrogen desorption; thus, only hydrogen desorption by back-formation of free sites is considered. The adsorption equilibria of chemisorbed hydrocarbon species and surface reactions of C_2H_2 , C_2H_3 , and C_2H_4 species can be expressed as

$$C_{\infty}() + C_2 H_2 \xrightarrow{k_{a_1}} C_{\infty}(C_2 H_2), \qquad [A2a]$$

$$C_{\infty}(C_{2}H_{2}) \xrightarrow{k_{+1} \gg k_{a1}} C_{\infty}(C_{2}H_{2}),$$
 [A2b]

$$C_{\infty}() + C_2 H_3 \xrightarrow{k_{a_2}} C_{\infty}(C_2 H_3), \qquad [A2c]$$

$$C_{\infty}(C_2H_3) \xrightarrow{k_{+2} \gg k_{a2}} C_{\infty}(H_3),$$
 [A2d]

$$C_{\infty}() + C_2 H_4 \xrightarrow{k_{a_3}} C_{\infty}(C_2 H_4), \qquad [A2e]$$

$$C_{\infty}(C_2H_4) \xrightarrow{k_{+3} \gg k_{a3}} C_{\infty}(H_4),$$
 [A2f]

$$C_{\infty}H_2 \xrightarrow{k_{d1}} C_{\infty}() + H_2,$$
 [A2g]

$$C_{\infty}() + H_2 \xrightarrow{k_{-d1}} C_{\infty}(H_2),$$
 [A2h]

$$C_{\infty}(H_3) \xrightarrow{k_{d_2}} C_{\infty}(\cdot) + \frac{3}{2}H_2,$$
 [A2i

$$C_{\infty}() + \frac{3}{2}H_2 \xrightarrow{k_{-d2}} C_{\infty}(H_3), \qquad [A2j]$$

$$C_{\infty}H_4 \xrightarrow{k_{d3}} C_{\infty}() + 2H_2,$$
 [A2k]

$$C_{\infty}(\)+2H_2 \xrightarrow{k_{-d3}} C_{\infty}(H_4).$$
 [A21]

Where $C_{\infty}() =$ free active site; $C_{\infty}(C_2H_2)$, $C_{\infty}(C_2H_3)$, $C_{\infty}(C_2H_4) =$ active sites with adsorbed hydrocarbon; $C_{\infty}(H_2)$, $C_{\infty}(H_3)$ $C_{\infty}(H_4) =$ active sites with adsorbed hydrogen, and k_{a1} , k_{+1} , k_{a2} , k_{+2} , k_{a3} , k_{+3} , k_{d1} , k_{d1} , k_{d2} , k_{d2} , k_{d3} , $k_{d3} =$ rate constants.

The rate equations of above adsorption and desorption reactions can be expressed as:

$$r_{a1} = k_{a1} C_{\infty}(\) p_{C_2 H_2}^{out},$$
[A3a]

$$r_{a2} = k_{a2} C_{\infty} p_{C_2 H_3}^{out},$$
 [A3b]

$$r_{a3} = k_{a3} C_{\infty}() p_{C_2 H_4}^{out},$$

$$r_{d1} = k_{d1}C_{\infty}(H) - k_{-d1}C_{\infty}()p_{H_2}^{out},$$
[A3d]

$$r_{d2} = k_{d2}C_{\infty}(H) - k_{-d2}C_{\infty}()p_{H_2}^{out},$$
 [A3e]

$$r_{d3} = k_{d3}C_{\infty}(H) - k_{-d3}C_{\infty}()p_{H_2}^{out}.$$
 [A3f]

The total concentration of active site, C, is the summation of that of free active site and active site with adsorbed hydrogen, that is

$$C = C_{\infty}(\) + C_{\infty}(H).$$
 [A4]

At steady-state conditions, the total adsorption rate is equal to the total desorption rate, and thus, we obtain

$$r_{a1} + r_{a2} + r_{a3} = r_{d1} + r_{d2} + r_{d3} = r_s,$$
[A5]

where $r_s =$ pyrocarbon deposition rate, which is proportional to the deposition rate of the carbon film, r_f . Substituting Eqs. A3a–A3f and A4 into Eq. A5, one obtains

$$r_s = r_f / k_4$$

$$=\frac{C(k_{a1}p_{C_{2}H_{2}}^{out}+k_{a2}p_{C_{2}H_{3}}^{out}+k_{a3}p_{C_{2}H_{4}}^{out})}{1+[(k_{-d1}+k_{-d2}+k_{-d3})p_{H_{2}}^{out}+(k_{a1}p_{C_{2}H_{2}}^{out}+k_{a2}p_{C_{2}H_{3}}^{out}+k_{a3}p_{C_{2}H_{4}}^{out})]/(k_{d1}+k_{d2}+k_{d3})},$$
[A6]

where k_4 is a constant. We had adopted Fourier transfer infrared (FTIR) spectroscope to measure the carbon films, and found that little hydrogen was within the carbon film. Hence, we believe that the hydrogen radicals $H \bullet$ in the carbon film is desorbed. The desorbed hydrogen radicals $H \bullet$ may be conjugated together to produce hydrogen gases H_2 , and then is exhausted to the atmosphere. Hence, we can predict that the rate constants of desorption, k_{d1} , k_{d2} , and k_{d3} , are much larger than that of adsorption. Accordingly, the second term on the denominator of Eq. A6 can be neglected. Therefore, Eq. A6 is reduced to

$$r_f = k_4 C (k_{a1} p_{C_2 H_2}^{out} + k_{a2} p_{C_2 H_3}^{out} + k_{a3} p_{C_2 H_4}^{out}).$$
 [A7]

The RGA results (as shown in Fig. A1) reveal that $p_{C_2H_2}^{out}$ or $p_{C_2H_3}^{out}$ is proportional to $(p_{C_2H_4}^{in})^{0.5}$, but $p_{C_2H_4}^{out}$ is proportional to $(p_{C_2H_4}^{in})^2$. Hence, based on Eqs. 1 and 4, we believe that k_{a3} is much larger than k_{a1} and k_{a2} , and thus, Eq. A7 can be further reduced to

$$r_f = k_4 k_5 C k_{a3} (p_{C_2 H_4}^{in})^2,$$
 [A8]

where k_5 is a constant. As stated in Eqs. 1 and 4, the deposition rate of carbon films is proportional to the partial pressure of the inlet gas C_2H_4 with a power of second order, and thus, the pyrolysis of C_2H_4 with added N_2 is resulted from the adsorption of the remaining precursor gases C_2H_4 on the silica glass plate substrate. Remarkably, the partial pressure of C_2H_4 , $p_{C_2H_4}^n$, in Eq. A8 is related to the $[C_2H_4/(C_2H_4 + N_2)-0.063]$ ratio in Eq. 1 and the working pressure $(p-p_c)/(p_0-p_c)$ in Eq. 4; the rate constant k_{a3} in Eq. A8 is related to the residence time $[\exp(q\tau)-\exp(q\tau_c)]$ in Eq. 2 and the temperature $\exp(-E/RT)$ in Eq. 3, and the total concentration of active sites *C* in Eq. A8 is dependent on the specific surface area of the substrate. In this study, the substrate surface will further diffuse and conjugate to form the laminar graphite structure.

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[A3c]

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