Characterization of a -C:H:N deposition from CH_4/N_2 rf plasmas using optical emission spectroscopy

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Optical emission spectra (OES) from CH_4/N_2 rf plasmas, which are used for the deposition of nitrogen-containing hydrogenated amorphous carbon (a -C:H:N) thin films, have been characterized. Previously unidentified spectral lines have been assigned to atomic N. Further identified species include CH, H, H_2 , N_2 , N_2^+ , N, and CN. Variations between spectra from the pure CH_4 or N_2 plasmas and the mixed CH_4/N_2 plasma are discussed. The enhancement of excited nitrogen species, with the addition CH_4 , is attributed to Penning ionization. The observed OES variations of the CH_4/N_2 plasma with power, pressure, and CH_4/N_2 ratio are explained in terms of possible reaction mechanisms and their activation, and correlated with preliminary film growth characteristics.

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I. INTRODUCTION

Amorphous hydrogenated carbon (a -C:H) films have received considerable attention over the last decade due to their unique “diamondlike” chemical, electrical, optical, and mechanical properties.^{1,2} Low-pressure rf plasma-enhanced chemical-vapor deposition (rf-PECVD) is one of the most widely used techniques, as it is possible to obtain films of widely varying properties depending on the plasma parameters used. The substrate negative self-bias, as influenced by the various parameters such as pressure, flow rate, power, etc., has been identified as the most critical in determining the final film characteristics, with hard carbon films being produced at moderately high bias voltages (400–600 V) and polymeric films at low bias voltages (<100 V).³

Further, the properties of the films are found to depend strongly on their microstructure, i.e., sp^3/sp^2 ratio and H content. As well as varying the hydrocarbon feedstock,⁴ additives such as hydrogen^{5,6} and the inert gases^{6–9} have been used in an attempt to further modify the structure of these films.

Recent interest surrounding the induced structural changes of nitrogen inclusion^{10,11} is due to the predictions of Liu and Cohen¹² that the bulk modulus of a hypothetical compound $\beta\text{-C}_3\text{N}_4$, structurally analogous to β -silicon nitride, may be close to that of diamond. Diamondlike carbon (DLC) films with both sp^3 and sp^2 bonding configurations are under varying degrees of compressive stress. It has been reported^{10,13,14} that the internal stress considerably decreases with the addition of nitrogen, without sacrificing hardness, up to a N incorporation of 2 at. %. At higher concentrations hardness is reduced due to the development of graphitic domains. Other workers have shown that nitrogen content increases with rising nitrogen partial pressure,^{10,13–18} with a concomitant reduction of hydrogen content^{13,14,17} and depo-

sition rate.^{16,17} Infrared studies^{13–15,17,19} indicate the development of CN and NH_2 groups. In terms of macroscopic film properties, it has been shown that nitrogen incorporation can cause a reduction of the electrical resistivity^{14,16,18,20} and optical band gap.^{14,16,18–20} From conductivity measurements, Amir and Kalish¹⁶ and Schwan *et al.*¹⁴ determined that nitrogen has a low doping efficiency in a -C:H films. Recent results,^{21–23} however, indicate that a -C:H:N is a superior electronic material to a -C:H. It is timely, therefore, to investigate the plasma activated processes which occur during rf-PECVD deposition of a -C:H:N films.

Further, studies to date have centered on the correlation of film properties with nitrogen partial pressure, the other deposition parameters being fixed. However, it is well known that with rf-PECVD-deposited undoped a -C:H,⁴ film structure depends strongly on the ion bombardment energy of the species involved in the film growth which is a function of the deposition parameters, particularly bias voltage. Thus, it is relevant to ascertain the effects of bias variations on film properties of a -C:H:N. In this article we report on the optical emission spectroscopy (OES) of CH_4/N_2 plasmas. The gas phase composition, i.e., the nature and concentration of various species, fragmentation of ions, degree of ionization, and gas phase collisions, all play a part in determining the nature of the resultant films. OES is a convenient and effective technique to detect and monitor a number of transient species such as excited atoms, ions, and molecules, with varying plasma parameters.

II. EXPERIMENT

The rf plasmas of CH_4 , N_2 , and CH_4/N_2 gas mixtures were generated in a 13.56 MHz capacitively coupled parallel plate electrode reaction chamber. The same configuration is used to deposit amorphous carbon films, details of which have been described previously.⁷ A commercial Verity Scanview OES system was used to collect the optical emission spectra. It incorporated an EP200 Msd Monochromator and R928HA photomultiplier tube detector. The spectra were collected from the rf plasmas through a quartz window in the

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FIG. 1. Typical optical emission spectra from (a) CH_4 , (b) N_2 , and (c) mixed CH_4/N_2 rf-PECVD plasmas.

plasma chamber wall. They represent an average of the observed plasma since localized fiber optic probes were not used in this instance. Emission spectra, in the range 300–900 nm, were collected for different plasmas generated by varying the plasma parameters as described below:

- (1) power (30–210 W), at fixed pressure (100 mTorr) and N_2/CH_4 ratio (0.25);
- (2) N_2/CH_4 ratio (0.1–2) at fixed power (30 W) and pressure (100 mTorr);
- (3) pressure (100–1000 mTorr) at fixed power (30 W) and N_2/CH_4 ratio (0.25).

III. RESULTS

Typical optical emission spectra of CH_4 , N_2 and CH_4/N_2 plasmas are shown in Figs. 1(a), 1(b), and 1(c), respectively. As reported in previous studies,^{24–26} the main emission peaks in the CH_4 spectrum [Fig. 1(a)] correspond to the CH 430 and 390 nm systems, and the hydrogen Balmer lines (H_α at

656 nm, H_β at 486 nm, and H_γ at 434 nm). Numerous H_2 molecular bands are also visible, particularly centered at 463 and 602 nm.

In the N_2 spectrum [Fig. 1(b)], a variety of nitrogen emission peaks span the measured spectral region. The four bands in the visible region, with bandheads at approximately 540, 580, 650, and 750 nm, are commonly associated with the first positive system of the neutral nitrogen molecule, these are thought to occur as a result of the recombination of ground-state nitrogen (^4S) atoms through a three-body collision process with a third body.²⁷ The peaks in the UV region centered at 316, 337, 380, 400, and 420 nm correspond to the most intense peaks of the second positive molecular series of neutral nitrogen and the sharp peaks at 391 and 428 nm are the most intense of the first-negative system of N_2^+ molecular ion transitions.^{28,29} Both these species can be produced by direct electronic excitation (ionization excitation) of ground-state N_2 molecules.^{29,30} Further, the second positive N_2 molecules may be generated by radiative recombination of an electron with an ionized N_2 molecule in its ground state.²⁹ These OES lines have been reported by other workers.^{30–32}

The sharp peaks rising above the first positive system at 631.3, 673.7, and 714.6 nm have been observed by Nam *et al.*³³ in a rf plasma of $\text{SiH}_4\text{--NH}_3\text{--N}_2$, but only identified as emission lines originating from various excited states of N_2 . Sharp bandheads in the near-IR (NI) spectral region centered at 745, 821, and 869 nm have been observed^{27,31} and identified as atomic nitrogen bands. The intensity of our lines leads us to believe that they are also due to atomic nitrogen transitions. Spectral lines are listed for atomic nitrogen at these wavelengths.^{34–36} There are allowed atomic NI transitions in the 627.5–632.2 nm range and 670.6–674.1 nm range. There is also a N II transition in the 713.9–725.7 nm range. The ionization energy for such species (25.1 eV) is, however, much higher than for N I (14.54 eV). The proportionality of the three lines remains constant regardless of the plasma conditions, thus we suspect that the three lines are due to N I.

In the CH_4/N_2 spectrum [Fig. 1(c)], lines due to CH_4 are almost completely obscured by those due to nitrogen. Further, in the mixed plasma there is the enhancement of the N_2 second positive bands relative to the N_2 first positive band, and the development of a band system with a bandhead at 388.3 nm which can be ascribed to CN. The CN violet system has three strong sequences with heads at 421.6, 388.3, and 359 nm (the 388.3 head being the strongest)²⁸ which have been observed by other workers.^{37–39} In our system, the 359 nm band is obscured by the strong N_2 second positive bands but when the 388.3 nm band is well developed, bands associated with the 421.6 nm sequence appear.

The energy level transitions and likely excitation processes for all the species described above are listed in Table I and their energy level diagrams are plotted in Fig. 2.

The CH (431.4 nm) band and the H_β (486.1 nm) band are not obscured by nitrogen peaks and have been monitored with the variation of plasma conditions. The CN peak (388.3 nm) and the strongest peaks due to the different nitrogen species were also monitored. These include the N_2 second positive peak at 357.7 nm, the N_2^+ peak at 391.0 nm, the N_2

TABLE I. Emission species in a CH₄/N₂ rf plasma.

Emission species	Energy level transitions	Wavelength ^a (nm)	Eq. no.	Excitation process	Threshold energy (eV)
CH	$B^2\Sigma \rightarrow X^2\Pi$	390			
CH	$A^2\Delta \rightarrow X^2\Pi$	430	(1)	$\text{CH}_4 + e \rightarrow \text{CH}^* + \text{H}_2 + \text{H} + e$	13.4 ^c
H _α	$3d^2D \rightarrow 2p^2P^0$	656	(2)	$\text{CH}_4 + e \rightarrow \text{CH}_3 + \text{H}^* + e$	21.9 ^c
H _β	$4d^2D \rightarrow 2p^2P^0$	486	(3)	$\text{H}_2 + e \rightarrow \text{H} + \text{H}^* + e$	17.25 ^c
H _γ	$5d^2D \rightarrow 2p^2P^0$	434	(4)	$\text{H} + e \rightarrow \text{H}^* + e$	13.06 ^c
H ₂	$G^1\Sigma_g^+ \rightarrow B^1\Sigma_u^+$	463	(5)	$\text{CH}_4 + e \rightarrow \text{CH}_2 + \text{H}_2 + e$	19 ^c
H ₂	$3p^3\Pi_u \rightarrow 2s^3\Sigma_g^-$	602			
N ₂	$B^3\Pi_g \rightarrow A^3\Sigma_u^+$	540, 580, 650, 750	(6)	$A^b + \text{N} + \text{N} = A + \text{N}_2^* = A + \text{N}_2 + e$	>9.76 ^d
1st positive N ₂	$C^3\Pi_u \rightarrow B^3\Pi_g$	316, 337, 357, 380, 400, 420	(7)	$\text{N}_2 + e \rightarrow \text{N}_2^* + e$	11.1 ^e
2nd positive			(8)	$\text{CH}_x^* + \text{N}_2 \rightarrow \text{CH}_x + \text{N}_2^* + e$	>14
N ₂ ⁺	$B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$	391, 428	(9)	$\text{N}_2 + e \rightarrow \text{N}_2^+ + 2e$	18.7 ^e
NI	$6s^4P \rightarrow 3p^4S^0$	631	(10)	$\text{N}_2^* + e \rightarrow \text{N} + \text{N} + e$	14.5 ^f
NI	$4d^4P \rightarrow 3p^4P^0$	673	(11)	$\text{CH}_x^+ + \text{N}_2 \rightarrow \text{CH}_x + \text{N} + \text{N} + e$	>15
CN	$B^2\Sigma \rightarrow X^2\Sigma$	422, 388, 359	(12)	$\text{CH}_x^* + \text{N}_2^* \rightarrow \text{CN} + \text{N} + \text{H}_y + \text{H}_z + e$	>14
			(13)	$\text{CH}_x^* + \text{N}_2^* \rightarrow \text{CNH}_y + \text{N} + \text{H}_z + e$	
			(14)	$\text{CNH}_y + A^* \rightarrow \text{CN} + A + \text{H}_x + \text{H}_\alpha + e$	
			(15)	$(x = y + z)(y = z + \alpha)$	

^aMost prominent peaks (to the nearest nm).

^bA is a participating species in a multibody collision process.

^cReference 24.

^dReference 29.

^eReference 30.

^fReference 36.

first positive peak at 661.3 nm, and the N peak at 673.7 nm. The variation in the intensity of these peaks, with increasing power, nitrogen flow rate, and pressure are plotted, using a log scale, in Figs. 3(a), 3(b), and 3(c), respectively.

FIG. 2. Diagram of energy level transitions for the observed OES lines.

With power [Fig. 3(a)] there is an increase in the intensities of all species, up to a saturation level, but the N₂⁺ and CN increases are greatest. With increasing N₂/CH₄ ratio [Fig. 3(b)] there is an initial increase in the intensity of all nitrogen derived species which levels off and this is accompanied by a corresponding initial decrease in the intensities of methane derived species (CH and H). With pressure [Fig. 3(c)] there is an initial decrease (from 100 to 400 mTorr) in the intensities of the OES lines of all the species. There is then an increase in the intensities of all species, apart from N₂⁺ (which levels off), up to 800 mTorr, with a further tailing off of all species at higher pressures.

IV. DISCUSSION

A. OES analysis

The most striking observations from this study are the previously unidentified sharp nitrogen spectral lines which we ascribe to atomic N, the development of CN bands, the enhancement of N₂ second positive spectral line intensities with the addition of CH₄, and the higher intensities of species originating from N₂ relative to those from CH₄. These points, together with the variation of spectral line intensities under different plasma conditions, are discussed below.

Until recently,³¹ atomic N had not been observed in a rf system. As the electron temperature T_e is greater in a microwave discharge ($T_e \sim 8$ eV) than in a rf discharge ($T_e \sim 3$ eV),⁴⁰ the nitrogen is expected to be more highly activated in a microwave discharge, leading to longer-lived atomic nitrogen atoms. In a rf discharge, nitrogen atoms would be expected to be shorter lived and to recombine rapidly into mo-

FIG. 3. Variation of optical emission intensities of species from N_2/CH_4 rf-PECVD plasmas, plotted on a log scale, as a function of (a) power (W), (b) N_2/CH_4 ratio, and (c) pressure (mTorr).

molecular nitrogen. Vaudo and co-workers,³¹ however, found that the intensity of atomic nitrogen peaks relative to the molecular bands was much stronger from a rf rather than a microwave source. The atomic nitrogen in their system, results from the dissociation of neutral (first positive) nitrogen. The atomic nitrogen lines in our system configuration and process window differ from those of Vaudo and co-workers; this could be a consequence of the higher intensities of second positive N_2 . Dissociative reactions [Table I, Eq. (10)] of this more energetic molecular nitrogen will result in atomic N with an increased lifetime of the higher energy levels and thus an increased probability of atomic transitions from these

levels. A further observation supporting this postulate is the fact that the intensity variations of these atomic nitrogen peaks mirror those of the second positive N_2 peaks under different conditions (Fig. 3).

Spectral lines due to CN are readily seen by OES,²⁸ due to its low activation energy (Fig. 2). It arises from the reaction of the active nitrogen species with carbon species in the plasma. A number of routes leading to its appearance has been reported.⁴¹ One route is the immediate formation of CN from chemical interaction between these species [Table I, Eq. (13)]. A further route is the initial formation of a stable intermediate compound containing C—N bonding which then yields CN on further reaction with active plasma species [Table I, Eqs. (14) and (15)].

Collisional interaction between plasma particles plays a significant role in activating reactive species. Penning ionization and dissociation processes [Table I, Eq. (8) and (11)] are especially effective in plasma excitation processes because they have large capture cross sections. It is known from mass spectroscopic studies^{42,43} that there are a number of excited C_mH_n species (ions and radicals) present in the plasma. These species tend to undergo collisional reactions, rather than deexcitation processes which result in OES lines, and could be acting as Penning agents in these nitrogen activation reactions, resulting in the promotion of the N_2 second positive bands. This enhancement was also observed by Sugimoto and co-workers,³² with the addition of helium to the nitrogen plasma. They suggested that molecules of N_2 in their ground state are not directly ionized by electrons in rf plasmas but excitation of nitrogen molecules occurs due to He Penning effects.

In a rf discharge the plasma is sustained by ions from the negative glow discharge diffusing to the glow-sheath boundary where they undergo acceleration, driven by the large electric field across the electrode sheath, and collide with the electrode surface with a high energy causing secondary electron and sputtered atom emission. The secondary electrons are accelerated back through the sheath and provide the primary energy feed to support the glow discharge ionization process, through direct ionization and charge transfer resulting from the high-energy tail of the emitted electron distribution. It has been reported^{44,45} that the magnitude of the ion energy, is dependent upon the sheath electric-field-to-pressure ratio (E/p) which also affects the optical emission intensity.

The relative emission intensity for a given transition ($i-j$) of a species X is given by the integral

$$I_{X(i-j)} = n_e N \int \left(\frac{2E}{m} \right)^{1/2} \sigma(E) f(e) dE, \quad (1)$$

where n_e is the electron density, N is the number density of the gas molecule, σ is the emission cross section (electron-impact excitation), E and m_e are the electron energy and mass, and $f(E)$ is the electron energy distribution function (EEDF). If it is assumed that the direct electron impact from the ground to the emitting state is the dominant excitation process, and that radiation is the dominant deactivation process, the intensity of the optical emission of a specie equates

directly to the associated impact inelastic collision reaction. The measured intensity of this emission line may be expressed by

$$I_X = C_X(E) \eta_X[X]. \quad (2)$$

The rate coefficient $C_X(E)$ is a function of the energy of the electrons which is affected by discharge parameters. It is directly proportional to E/p . The excitation efficiency [$\eta_X = k_e(E)n_e$] is a function of the density and energy distribution function of the electrons, since $k_e(E)$ is the excitation rate constant, and n_e is the electron density. The concentration of the reactant species is given by $[X]$.

The fact that the relative intensities of OES active plasma species derived from N_2 are much higher than for the species derived from CH_4 , even though the activation energy of CH is low (Fig. 2) can be explained with reference to Eq. (2). The rate coefficient $C_X(E)$ is constant since the plasma parameters are fixed and the concentration of CH_4 is higher than that of N_2 . The difference in band intensities of species from N_2 and CH_4 must, therefore, be due to a higher excitation efficiency η_X of N_2 relative to CH_4 . This reflects the fact that the nitrogen species are principally generated by primary electron excitation [Table I, Eqs. (7), (9), and (10)], whereas the methane species are generated through secondary collisional processes [Table I, Eqs. (1)–(5)].

The increase in the intensities of all species with power [Fig. 3(a)], up to a saturation level, can also be explained by referring to Eq. (2). DebRoy, Kumar, and Tankala⁴⁶ showed that electron temperature increases with bias voltage and that electron density increases with an increase in electron temperature. Under our conditions (30–210 W), at fixed pressure the bias voltage increases from -30 to -300 V, thus, the rf field strength (and therefore C_X) will increase resulting in an increase in electron temperature T_e and electron density. This will cause an increase of all reaction processes and thus an increase in the intensities of all the observed optical emission bands, up to a saturation point, after which further increases in T_e will cease to influence the electron density. The fact that the N_2^+ intensities increase more steeply than the other species of N_2 is due to its higher activation energy for direct electron impact excitation. The CN species, on the other hand, result from dissociative excitation processes [Table I, Eqs. (13)–(15)] which have higher activation thresholds than direct excitation processes.

It can be seen [Fig. 3(b)] that as the N_2 partial pressure increases, there is an initial increase in the emission intensity of nitrogen species, including CN, with a corresponding decrease of CH and H intensities. These trends level off at higher N_2 concentrations. This is expected since the concentration of N_2 molecules [$[X]$ in Eq. (2)] and, therefore, their capture cross section has increased. As all other parameters are fixed, this increase will, however, be finite since there is a limited electron density. The slight decrease in CH and H intensities could be due to further interactions of N_2 and CH_4 derived species.

With pressure [Fig. 3(c)], there is an initial decrease in the optical line intensities of all species followed by a further increase in intensity for all species apart from N_2^+ , then a tailing off of all species at higher pressures. An increase in

pressure will cause a decrease in the bias voltage, and, therefore, electron temperature and electron density. Referring back to Eq. (2) it will also decrease the rate coefficient for direct electron impact excitation processes. The initial decrease is likely to reflect this reduction in T_e . On the other hand, the mean free path decreases with increasing pressure, resulting in an increase in the cross sections of collisional interactions and therefore the population of excited states for the various species present in the plasma. This population increase promotes a corresponding increase in the emission intensity of the plasma, but this effect is finite. As the electron temperature and density continue to decrease, the bulk electrons have insufficient energy to sustain these competitive collisional and charge transfer processes. The fact that the N_2^+ does not show this increase tends to confirm the above observation that it is produced exclusively from direct bulk electron impact excitation.

It is believed that the competitive collisional and charge transfer processes described above, conspire to promote the observed spectral intensity signal peak-to-trough transition shown in Fig. 3(c), close to 500 mTorr. To a first order, it is reasonable to propose that changes in mean free path, electron energy distribution and efficiency, and ionization type and efficiency, resulting from varying the total operating gas pressure (hence mean free path and reaction cross sections) and the plasma frequency and power, will promote the inverted S-shaped intensity curves observed.

B. Film growth

It is well known³ that the properties of a -C:H films, deposited using a self-negatively biased rf-PECVD system, depend strongly on the deposition parameters. The key parameter in determining the material properties, i.e., sp^3 bonding, film density, and hydrogen concentration, is the bombardment ion energy. This is a function of the self-bias voltage, which in turn is a function of the rf power coupled into the plasma.⁴⁷ According to models for sp^3 -rich a -C formation,^{47,48} at moderate ion bombardment energies (~ 50 – 200 eV) the subsurface penetration by energetic ions can lead to densification or, from an alternate viewpoint, increase film stress. The densification/stress increase can in turn promote metastable sp^3 bonding in the films.^{48,49} Energetic ion bombardment of the surface causes sputtering and lowers the H content and affects the growth rate.

As mentioned above, the magnitude of the ion energy and influence is dependent upon the sheath electric-field-to-pressure ratio E/p . The electric field is directly proportional to the self-bias voltage V_b which increases with power and decreases with pressure. At a fixed pressure, an increase in power increases the ion energy and fluence, due to the increased electric field,⁴⁴ as a direct consequence of the increase in the electron temperature and electron density. For a given driven electrode power, an increase in pressure causes a decrease in electric field and therefore plasma electron temperature and density which results in a lower bombardment energy and fluence. With increasing pressure, there is also an increase in the average collision rate (reduced mean free path), which will further affect the ion energy and fluence. Moreover, Economou and co-workers⁴⁵ observed that the

charged particle density exhibits a sharp decrease at lower pressure promoting a similar response from the ion fluence. Further, Catherine⁴⁴ observed that although ion bombardment is the key parameter in determining the film microstructure, by influencing densification, sputtering, and forward transport effects, adsorption of the plasma-dissociated active species follows a $P^{-0.5}$ law and governs the growth kinetics.

In interpreting the effect of a -C:H:N film properties with changes in the plasma parameters and correlating them to the observed changes in the OES spectra, these effects have to be considered. We have found that for the deposition of a -C:H:N films the growth rate, at constant power, is lower than for the a -C:H films deposited from pure methane, and that as the power (bias voltage) is increased, the growth rate decreases to a point where no growth is observed. A reduction in deposition rate has also been reported with rising nitrogen partial pressure.^{16,17} We have also observed that with increasing pressure, there is a trough-peak-trough growth regime.

It is not possible to monitor all the active C_mH_n species using OES; however, the results indicate that reactive nitrogen species are more easily generated than methane-derived species. Nitrogen can be introduced into the films either through the generation of active C_xN_y -containing species in the plasma or at the growth surface. The observation of CN peaks in the OES suggest that generation of active CN species does take place in the plasma under the experimental conditions observed.

Several factors may be contributing to the observed reduction of the growth rate of the films with the inclusion of nitrogen. As stated above, nitrogen species appear to be more reactive than the CH_4 precursor species, therefore, an increased flux of nitrogen in the plasma will result in a dilution of CH_4 precursor species and their collisional reactions. This will cause a reduction in the concentration of the molecular $C_mH_n^*$ species necessary for film formation. The observation that the CN OES peak develops while the CH peak decreases, with increased nitrogen partial pressure [Fig. 3(b)], suggests that this occurs.

As power, and therefore bias, increases the ion bombardment energy and ion flux increases, resulting in a higher sputter yield. The OES shows high concentrations of nitrogen species (especially N_2^+). The experimental data suggest that in this regime the arrival energy and flux of N_2^+ is sufficient to effect sputter etching. This sputter etch process is likely to be of a chemical/physical nature, much as the effect of hydrogen.^{5,6}

In the low-pressure (100 mTorr) high- V_b regime, the low growth rates can be explained by the high sputter yield of N_2^+ , as described above. At intermediate pressure (400 mTorr), it can be seen from the OES that the concentration of nitrogen species has dropped. Preliminary results show that the deposition rate and nitrogen inclusion (infrared) increases in this regime. The increase in deposition rate, as pressure increases and bias voltage decreases, could be due to a reduction in the arrival ion energy and consequently, the influence of the N_2 ion-induced sputter yield.

In the high-pressure (800 mTorr) low-bias regime, the OES [Fig. 3(c)] shows that the concentration of N_2^+ does not increase as do the other N_2 -derived species. The arrival ion energy will be very low and N_2^+ sputter etching will be much reduced. There is, however, a drop in film deposition rate due to the ion energy and fluence at the surface being low.

V. CONCLUSIONS

The optical emission spectra of CH_4/N_2 13.56 MHz, rf plasma discharges, used for the deposition of a -C:H(N) films, have been studied. Emission peaks due to CH, H, and H_2 are observed for CH_4 , and peaks due to molecular N_2 first positive, N_2 second positive transitions, and N_2^+ are observed for N_2 . We have also observed emission peaks which can be assigned to atomic N derived from higher-energy transitions resulting from the dissociation of the N_2 second positive molecules. In the mixed CH_4/N_2 plasmas, emission peaks due to CN have been identified and suggest that plasma reactions are important in the growth of a -C:H:N films. The intensities of the lines due to N_2 species are much higher than those due to CH_4 species. This reflects the fact that the activation energies for the generation of energetic nitrogen species are lower than for methane-derived species. The enhancement of the N_2 second positive intensities, with added methane, have been ascribed to Penning ionization processes induced by interaction on N_2 with $C_mH_n^*$ species in the plasma.

The variations in the optical emission intensities of the observed plasma species, that are induced by changes in the plasma processing parameters (i.e., power, N_2 partial pressure, total pressure), can be explained in terms of modifications to electron temperature and density, reactive species concentrations, and their associated arrival fluxes and activity states. Further, these can be correlated to film growth rates. Particularly, the decrease in film growth rate with increasing power (bias voltage), to a point where there is no film growth, is considered to be due to the increasing energetic N_2^+ acting as an efficient chemical/physical sputter agent. Due to the complexity of the relationship between the plasma parameters and the emission spectra, these observations are qualitative in nature. Further work in this area needs to be based on a quantitative interpretation of the emission spectra and correlation with other measurements of the plasma parameters.

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