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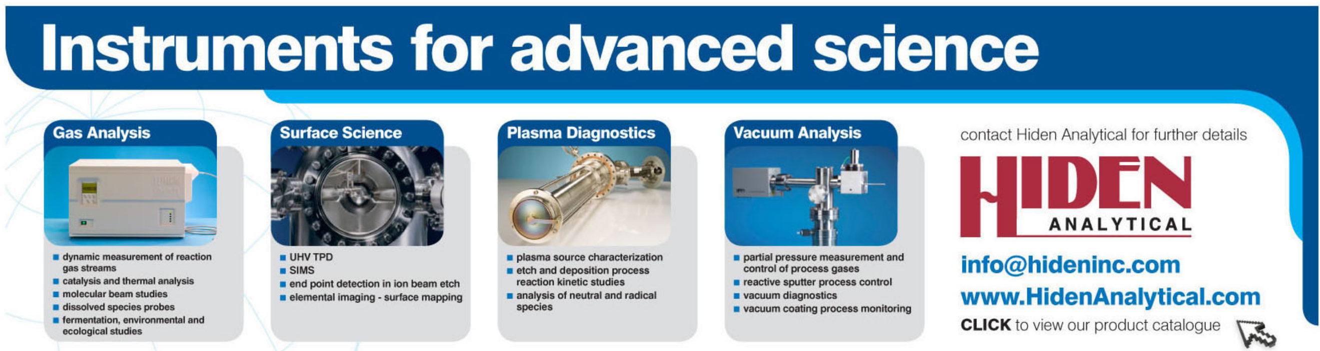

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Optical emission study of reaction mechanisms in the deposition of nitrogen-containing amorphous hydrogenated carbon films

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The reaction mechanisms taking place in a film-forming radio frequency discharge of a mixture of acetylene, nitrogen, and helium have been investigated using optical emission spectroscopy. A transient actinometric method was employed, based on the interruption of the flow of one of the feed gases (either C_2H_2 or N_2), and the subsequent observation of the time-dependent changes in the discharge environment, specifically of the concentrations of CH and CN species, two possible precursors of film formation. Both N_2 and C_2H_2 affect the CH and CN concentrations. Nitrogen strongly enhances the rate of formation of CH, very probably via gas phase reactions between atomic nitrogen and C_2H_2 or other species containing carbon and hydrogen. On the other hand, the relatively high CH concentration observed in discharges without nitrogen is taken to indicate that fragmentation of the C_2H_2 molecules by the discharge is another important mechanism of formation of the CH species. For the CN species, gas phase reactions between carbon- and nitrogen-containing species are expected to contribute to its appearance. However, a relatively high CN concentration could be detected even in discharges without C_2H_2 in the gas feed, so long as a nitrogen-containing polymer film was previously formed on the inner wall of the chamber. This is taken as evidence that interactions between the plasma and the polymer surface play an important role in the generation of the CN species. Further measurements of the CN concentration in a plasma of 100% He, produced in the chamber immediately after the formation of a nitrogen-containing polymer film, indicate that a possible reaction mechanism for the formation of the CN species is the detachment of nitrile groups (—C≡N) from the polymer surface upon cleavage of the carbon bond linking the nitrile terminations to the polymer chains. © *1995 American Vacuum Society.*

I. INTRODUCTION

In the last few decades, the technique usually known as plasma enhanced chemical vapor deposition (PECVD) has proven very useful for the deposition of thin films with diverse chemical compositions and a range of practical applications. The use of organic compounds as starting materials, or *monomers*, in the deposition discharge, results in materials whose structures range from that of an organic polymer[1] to that of a carbonaceous substance,[2] depending on the deposition parameters such as the power applied to the discharge, the system pressure, and the substrate temperature.

Addition of noble or reactive inorganic gases to the organic component in the discharge strongly influences the deposition rate, structure and physical properties of the film. While noble gases such as Ar and He are usually employed as *plasmogenic* gases,[3] i.e., as substances that do not enter into the film composition, but increase the plasma electron temperature and density, reactive inorganic gases added to the organic gas directly alter the chemical composition of the deposited material. Films grown from discharges of mixtures of various hydrocarbons with H_2 (Ref. 4), N_2 (Ref. 5), CO (Ref. 6), and SF_6 (Ref. 7) are examples of materials whose composition is modified by the inorganic component.

Recently, films deposited by PECVD in hydrocarbon–nitrogen mixtures have received renewed attention. One of the motivations for the study of these materials—usually known as amorphous hydrogenated nitrogenated carbon (*a*-C:H:N) films—is the possible improvement in the physical properties of hydrogenated amorphous carbon (*a*-C:H) by the addition of nitrogen. Supposedly, the incorporation of nitrogen adds extra π electrons which modify the thermostability[8] and mechanical properties of the films. Indeed, nitrogenated carbon may form a phase with a hardness comparable to that of diamond.[9] On the other hand, the optical band gap[10] and electrical conductivity[11] of *a*-C:H:N films can be modulated by their nitrogen content and this suggests applications in electronic and optoelectronic devices. Another important aspect of *a*-C:H:N films is related to the physicochemical properties of the film surface: nitrogen forms polar functional groups (amines and nitriles) in the deposited material, greatly improving the wettability of the film surface and its bondability to other materials.[12]

Despite the many studies undertaken to date on materials deposited by PECVD from hydrocarbon–nitrogen mixtures, much remains to be learnt on the inter-relationship between film structure and the discharge environment. Indeed, current understanding of the reaction mechanisms in these discharges could be much improved. In view of this, we have recently employed infrared and optical emission spectroscopies in a study of plasma polymerization in C_2H_2–N_2–He mixtures.[13] In that study, the procedure suggested by Coburn and Chen,[14] now widely known as the *actinometric technique*, was used, whereby the relative concentrations of two gas phase chemical species—CH and CN, which are possible precursors of film formation—were determined as a function of a key system parameter, namely, the percentage of nitrogen in the gas feed.

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In the present article, actinometry was again employed in studies of discharges of C_2H_2, N_2, and He mixtures but in this case was used to delineate transient concentrations of CH and CN in the discharge, caused by the interruption of the flow of one of the gas components (N_2 or C_2H_2). From these data, clues to reaction mechanisms in the discharge and on the growing polymer surface were obtained.

II. EXPERIMENT

The deposition chamber, pumping system, gas flow assembly, and optical spectroscopy apparatus have recently been described in detail.[13] In summary, the discharges were produced in a stainless steel chamber fitted with horizontal parallel plate electrodes capacitively coupled to a radiofrequency power supply (40 MHz, 100 W). Acetylene, nitrogen, helium, and argon were fed to the chamber via mass flow controllers. During the experiments, the chamber was pumped continuously by a two-stage rotary pump. All the experiments were carried out at a rf power of 70 W and at a total pressure in the chamber of 9–13 Pa.

A 1-m-focal length monochromator spectrometer was employed to identify characteristic peaks from species emitting from the region between the two electrodes. The optical grating used had 1200 lines/mm and was blazed at 500 nm. Since the reciprocal linear dispersion was about 0.8 nm/mm in the range of wavelengths measured, and the slit width was 150 μm, the resolution was about 0.12 nm.

To determine the relative concentrations of CH and CN, respectively, [CH] and [CN], the actinometric technique was employed and Ar or He or N_2 was used as an actinometric gas. The wavelengths of the optical emissions monitored were: 431.4 nm (CH), 385.1 nm (CN), 382.0 nm (He), 430.0 nm (Ar), and 337.1 nm (N_2). Since this work concerns transient concentrations, both [CH] and [CN] were calculated as a function if time by the equation

$$[X(t_i)]=kI_X(t_i)/I_A(t_i), \quad (1)$$

where X is either CH or CN, k is a constant and $I_X(t_i)$ and $I_A(t_i)$ are, respectively, the intensities of the species X and of the actinometer at time $t=t_i$. The values $I_X(t_i)$ and $I_A(t_i)$ were measured, respectively, from the intensity curves $I_X(t)$ and $I_A(t)$, taken with a strip chart recorder in two experiments sequentially performed under identical conditions.

A necessary condition for the correct application of Eq. (1) is that the concentration of the actinometer in the discharge is constant, and this was the case in our experiments. Ideally, the threshold energies for the electronic transitions to the states that give rise to the characteristic emissions of the species of interest and the actinometer should be the same. In addition, the excitation efficiencies of the two species should have a similar dependence on the plasma parameters, particularly the electron temperature, and it is well known that this condition is often met in practice. However, the condition of identical threshold energies is rarely met because there are not many candidates for actinometric gases. Consequently, in our experiments, Ar, He, and N_2 were used even though their threshold energies 14.5, 24.2, and 11.2 eV, respectively, differ from those of CH ($\cong$11 eV) and CN (3.2 eV).

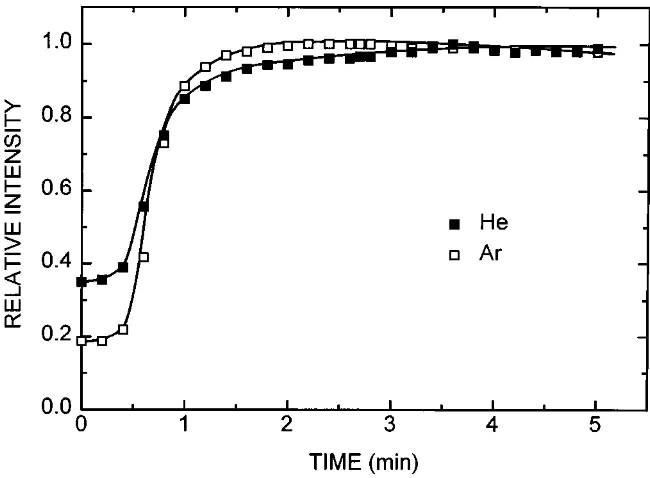

FIG. 1. Relative emission intensities of He and Ar as a function of time following the N_2 flow cutoff in a discharge of C_2H_2, He, and Ar mixture. The N_2 flow was cut at $t=0$ min. Gas flows: 1.5 sccm (C_2H_2), 3.5 sccm (He), and 0.5 sccm (Ar). Nitrogen flow before cutoff: 3.0 sccm.

Owing to the assumptions made here, only *trends* in the concentrations of plasma species are obtained. However, this restriction applies equally to all previous reports of actinometric data obtained by this method from polymerizing discharges.

III. RESULTS AND DISCUSSION

A. Dynamic actinometry of the C_2H_2–N_2–He system

Figure 1 shows the self-normalized emission intensities of Ar and He as a function of time from a plasma of a C_2H_2, He and Ar mixture. Nitrogen was also present in the mixture up to a time arbitrarily set to $t=0$ min, when the nitrogen flow was cut. Both intensity curves rise steeply as N_2 is pumped from the discharge and subsequently stabilize. Thus N_2 has a cooling effect on the discharge; reduction of the N_2 flow increases the plasma activity. As the thresholds for the emissions of Ar and He differ widely in energy (14.5 and 24.2 eV, respectively), all the free electrons of the discharge within this range are strongly and similarly influenced.

A second set of self-normalized emission intensities for Ar and He as a function of time are shown in Fig. 2. These emissions are now from a discharge of a N_2, He, and Ar mixture. Acetylene was initially present in the mixture and at $t=0$ min the C_2H_2 flow was cut. The decay of both intensity curves as C_2H_2 is pumped from the chamber shows that C_2H_2 has an effect opposite to that of N_2, increasing the plasma activity, A. As defined previously,[7] $A=\rho E$, provided ρ is the mean electron density and E is the mean electron energy. Thus if A increases, either ρ or E increases (or both increase). From Figs. 1 and 2 it can be seen that constant Ar and He intensities are reached at most about two minutes after the N_2 or C_2H_2 feed is interrupted. This is the time taken to pump the bulk of these gases from the chamber.

Figures 3 and 4 show the relative concentrations of the species CH and CN in the plasma, as a function of time following interruption of either the N_2 or the C_2H_2 feed. As

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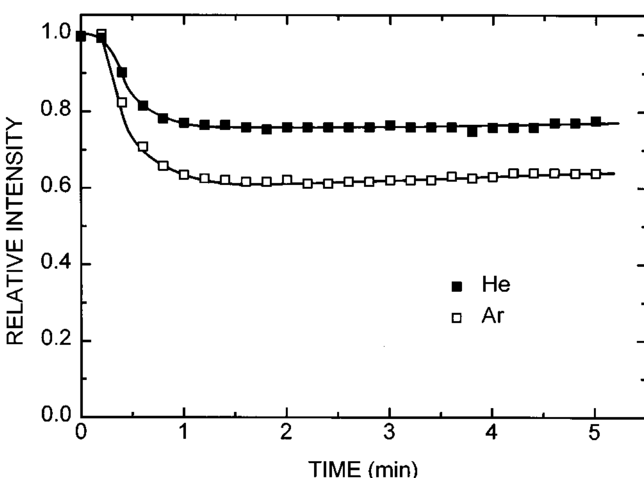
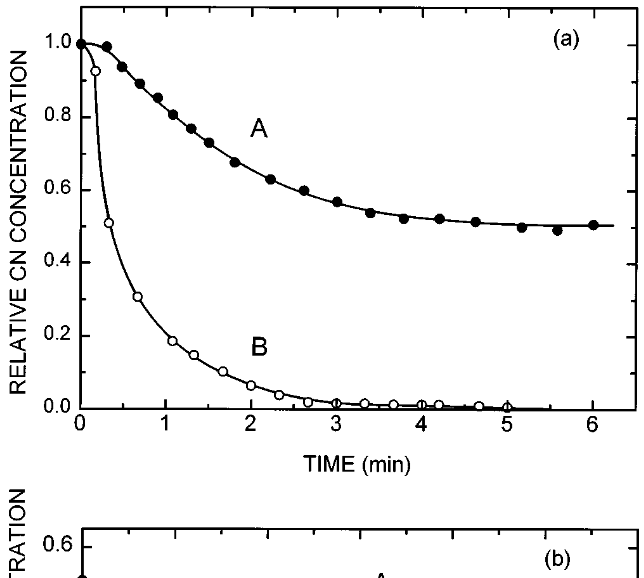


FIG. 2. Relative emission intensities of He and Ar as a function of time following the C_2H_2 flow cutoff in a discharge of N_2, He, and Ar mixture. The C_2H_2 was cut at $t=0$ min. Gas flows: 3.0 sccm (N_2), 3.5 sccm (He), and 0.5 sccm (Ar). Acetylene flow before cutoff: 1.5 sccm.



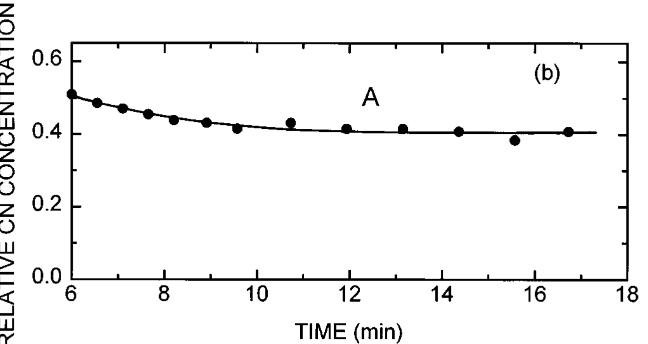


FIG. 4. (a) Relative concentration of species CN in the discharge as a function of time following the C_2H_2 flow cutoff (curve A) and N_2 flow cutoff (curve B) at $t=0$ min. Gas flows for curve A: 3.0 sccm (N_2), 3.5 sccm (He), and 0.5 sccm (Ar); C_2H_2 flow before cutoff: 1.5 sccm. Gas flows for curve B: 1.5 sccm (C_2H_2), 3.5 sccm (He) and 0.5 sccm (Ar); N_2 flow before cutoff: 3.0 sccm. (b) Continuation of curve A. Argon was used as the actinometer.

in the previous experiments, before interruption, the chamber was fed with a mixture of C_2H_2, N_2, He, and Ar.

As can be seen from curve A, in Fig. 3, after the N_2 supply is cut, at $t=0$ min, [CH] falls very rapidly to about half of its former value. This is despite of the increase in the plasma activity observed in the absence of N_2. Thus nitrogen must play a key role in the generation of CH. In fact, most organic substances react vigorously with excited nitrogen molecules and nitrogen atoms produced in a glow discharge.[15] With a few exceptions, organic compounds are destroyed on contact with atomic nitrogen, forming hydrogen cyanide, cyanogen, ammonia, and low molecular weight gases. Reactions between acetylene and nitrogen have been studied by several investigators[15] and hydrogen cyanide is usually reported as an abundant reaction by-product.[16–19] A possible reaction leading to CH is

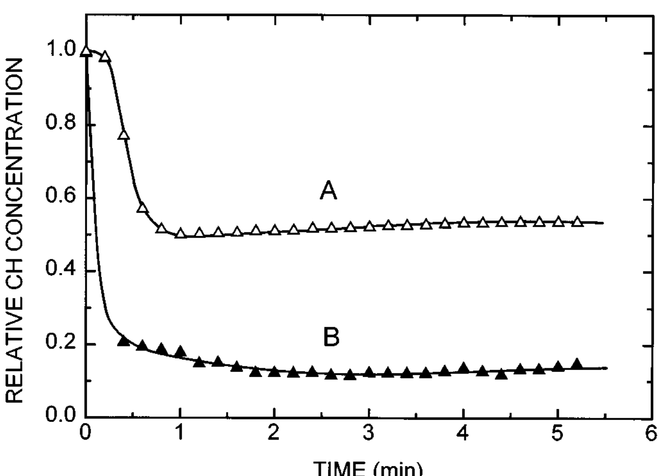


FIG. 3. Relative concentration of species CH as a function of time following the N_2 flow cutoff (curve A) and the C_2H_2 flow cutoff (curve B) at $t=0$ min. Gas flows for curve A: 1.5 sccm (C_2H_2), 3.5 sccm (He), and 0.5 sccm (Ar); N_2 flow before cutoff: 3.0 sccm. Gas flows for curve B: 3.0 sccm (N_2), 3.5 sccm (He), and 0.5 sccm (Ar); C_2H_2 flow before cutoff: 1.5 sccm. Argon was used as the actinometer.

$$N+C_2H_2 \rightarrow HCN+CH. \quad (2)$$

The large variety of reactive species in the discharge allows other possibilities. As suggested by other investigators,[19] a methylene radical may be formed by the reaction

$$N+C_2H_2 \rightarrow CN+CH_2. \quad (3)$$

In our discharge, the CH species may then arise from electron detachment of a hydrogen atom from the CH_2 radical.

It should be pointed out, however, that even though very important sources of the CH radical are reactions involving nitrogen species, the nearly constant [CH] level observed in Fig. 3 when N_2 is absent from the chamber, can be, at least in part, attributed to fragmentation of the acetylene molecules by the electrons of the discharge. On the other hand, since He metastables formed in a glow discharge may have energies exceeding the energy of the carbon triple bond in the C_2H_2 molecule (10 eV), a Penning dissociation reaction,

$$He^{*}+C_2H_2 \rightarrow 2CH+He, \quad (4)$$

where the asterisk (*) indicates a metastable state, is likely to occur, contributing to the concentration of CH in the discharge.

The change in the relative concentration of the species CH with time, when the flow of C_2H_2 was interrupted, is also

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shown by the curve B, in Fig. 3. The steep decline in [CH], following the flow interruption at $t=0$ min, is due to the decrease in the supply of CH units (in the form of C_2H_2). The decrease in the plasma activity, following the removal of C_2H_2 from the reactor, also contributes to the reduction in the CH concentration. However, [CH] does not fall to zero after the C_2H_2 flow is cut but remains nearly constant at about 10% of its initial value. This suggests that C_2H_2 remains in the chamber after the flow is interrupted. A tentative explanation for this residual effect is based on a possible release of C_2H_2 molecules previously absorbed by the polymer coating formed on the inner surface of the chamber during deposition. In fact, Zabolotny *et al.*[17] reported that C_2H_2 was apparently incorporated into the polymer film formed during reactions between C_2H_2 and nitrogen. When the polymer film reacted with active nitrogen, part of the C_2H_2 supposedly decomposed by the preceding reaction was recovered. Since in our data the residual level of [CH] is very low, this would imply a small residual partial pressure of C_2H_2.

The time evolution of [CN], after the C_2H_2 flow cutoff, at $t=0$ min, is represented by the curve A in Figs. 4(a) and 4(b). A slow decrease in [CN] follows the flow interruption, the [CN] leveling off at a concentration of about 40% of the initial value. This high "residual" concentration is rather surprising if we assume that the CN radical arises from gas phase reactions between nitrogen and C_2H_2 molecules or its fragments. Even if the release of C_2H_2 molecules by the polymer coating actually takes place, as discussed in the previous paragraph, the resulting C_2H_2 partial pressure would be too small to account for the large values of [CN] at the tail end of the curve of Fig. 4(b). This behavior strongly suggests that gas phase reactions are not the only source of the CN species; interactions between plasma species and the polymer film deposited on the inner surface of the chamber may also account for the presence of the CN species in the discharge.

In view of the above data for [CN], we may consider the total rate of formation of CN, R_{CN}, (in units of number of particles formed per unit time) as the sum of the rates due to gas phase and surface reactions, respectively $R_{CN}(g)$ and $R_{CN}(s)$. Significant clues as to the relative importance of $R_{CN}(g)$ and $R_{CN}(s)$ on the total rate R_{CN} can be drawn from curve A in Fig. 4. The decrease in [CN] following the C_2H_2 flow cutoff suggests that gas phase reactions are important in the formation of the CN radicals. However, since [CN] remains at a relatively high level after the C_2H_2 flow is cut, even though the plasma activity decreases, this strongly indicates that surface reactions play a significant role in the generation of the CN species in discharges of C_2H_2, N_2, and He mixtures.

While both gas phase and surface reactions are important for the generation of the CN species, we have no conclusive evidence of surface reaction mechanisms involved in the formation of the CH species. However, even if the residual CH concentration (Fig. 3, curve B) is in fact due to surface reaction mechanisms, these do not contribute significantly to the CH concentration in the discharge.

It is also of interest to observe the time dependence of the CN concentration in a discharge initially containing C_2H_2, N_2, He, and Ar, after the feed of N_2 is cut at $t=0$ min. As shown by the curve B in Fig. 4(a), [CN] is rapidly depleted as N_2 is pumped from the chamber, and for practical purposes vanishes at about 3 min. The disappearance of the CN signal following the N_2 flow cutoff provides further confirmation that CN species can be generated from reactions on the polymer surface. As polymerization of C_2H_2 continues to occur when N_2 is absent from the discharge, a film containing only C and H is formed on top of the nitrogen-containing film previously deposited on the walls of the chamber. This new material acts a passivation layer, protecting the underlying nitrogen-containing film from further interactions with the plasma.

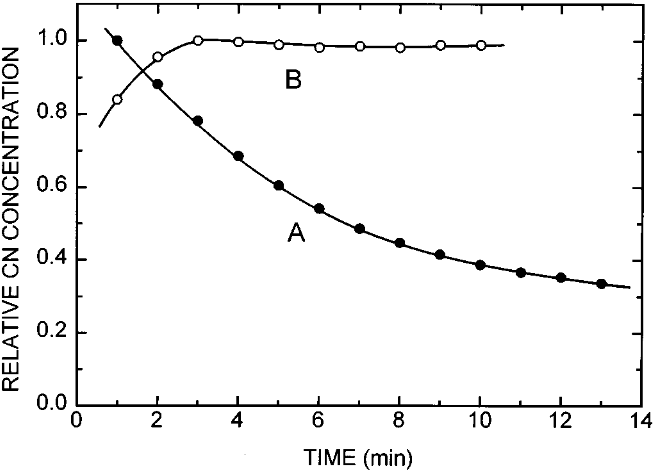

FIG. 5. Relative concentration of CN species as a function of time in plasmas of 100% He (8.0 sccm, curve A) and 100% N_2 (8.0 sccm, curve B) after a 10 min discharge with the following gas flows: 1.5 sccm (C_2H_2), 3.0 sccm (N_2), and 3.5 sccm (He).

B. Possible surface reaction mechanisms

To investigate possible reaction mechanisms on the surface of the polymer film formed on the inner surface of the chamber, we performed experiments in which [CN] was measured as a function of time in plasmas of 100% helium and 100% nitrogen initiated in the chamber immediately after a film-forming discharge in a C_2H_2, N_2, and He mixture for a time T. The relative CN concentrations were determined by Eq. (1). For 100% He and 100% N_2 discharges, He and N_2 were respectively used as actinometers. The results are illustrated by the curves of Fig. 5. The measurements for each one of the curves were preceded by a discharge in the gas mixture during $T=10$ min. As shown in Fig. 5, for the He plasma (curve A), [CN] decays with time and after 12 min is reduced to about 33% of its initial value. In the discharge of N_2 (curve B), [CN] initially increases, and at about 3 min after the discharge is initiated remains nearly constant. According to our previous discussion, if C_2H_2 is absent from the discharge, the gas phase CN species arises from plasma–polymer surface interactions in both helium and nitrogen discharges.

A number of such interactions have frequently been observed at plasma–polymer interfaces. In fact, during the course of a PECVD process, the growing film surface is

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continuously bombarded by UV radiation, electrons, ions and neutral species in metastable and ground states. Breaking of covalent bonds[20,21] on the polymer surface, crosslinking[22] and a variety of surface reactions result from these interactions. A commonly observed effect on polymer surfaces treated by plasmas is the creation of new functional groups by incorporation of reactive species from the discharge.[23–26] On the other hand, in glow discharges like those of H_2, Ar, and He, species may be found in metastable states with energies exceeding bond energies in the polymeric chains. Bond cleavage and the subsequent reorganization of the surface chemical structure may result from the release of metastable energies to the surface macromolecules.[23]

Considering that nitrile functional groups (—C≡N) are present in films deposited from plasmas containing hydrocarbons and nitrogen,[5,8,10,27] a possible explanation for the appearance of the CN species in the He plasma is the cleavage of the carbon bond linking the nitrile termination to the polymer chain, upon the release of energy from plasma species, and the subsequent desorption of the CN fragment. Such a plasma-induced desorption (PID) mechanism would more likely involve nitrile rather than other functional groups containing nitrogen (e.g., amines), since in the former a single C–C bond would have to be broken to produce desorption of the CN particle. While high kinetic energy electrons and ions may produce CN desorption, the effect of metastable He atoms on the polymer surface should not be disregarded as the metastable He energy (19.8 eV) exceeds the energy of any bond in the polymer chains.

It should be noted that the decay of [CN] during the He discharge, shown in Fig. 5, is consistent with these ideas. If the CN species are desorbed from the polymer film, a decrease in [CN] is indeed to be expected as a consequence of the depletion of CN units at the polymer surface.

It seems reasonable to suppose that the PID mechanism also accounts for the appearance of CN in the nitrogen plasma because plasma species such as ions and electrons may have energies exceeding that of the C–C bond linking the nitrile groups to the surface macromolecules ($\approx$6 eV). The effect of metastable atoms on the polymer surface may now be disregarded, because of the low metastable nitrogen atom energy (2.38 eV). However, since nitrogen from the nitrogen discharge may be incorporated into the polymer film, a fraction of the detected CN species may arise from CN units (possibly nitrile functionals) previously formed on the film surface by the action of the nitrogen plasma itself. In fact, the behavior of [CN] with time, illustrated in Fig. 5 for the nitrogen plasma, suggests that initially (0–3 min), a growing number of CN bonds is formed on the polymer surface, giving rise to an increasing gas phase CN concentration. After about 3 min, a steady state condition is reached in which the number of CN units formed per unit time on the polymer surface equals that of CN species detached.

In another set of experiments, plasmas of 100% He and N_2 were established immediately after 10 min discharges containing only a mixture of C_2H_2 and He. The feed gas flows were 1.5 and 6.5 sccm for C_2H_2 and He, respectively. In the 100% He (8.0 sccm) discharge following the discharge in the mixture for 10 min, the CN emission signal could not be distinguished from background. This is to be expected because in this case the film does not contain nitrogen and therefore cannot yield CN particles. However, in the 100% nitrogen discharge, also following a 10 min discharge in the mixture, the CN emissions was again clearly detected and [CN] evolved with time as shown in Fig. 6. As before, [CN] was calculated by Eq. (1), using N_2 as the actinometer.

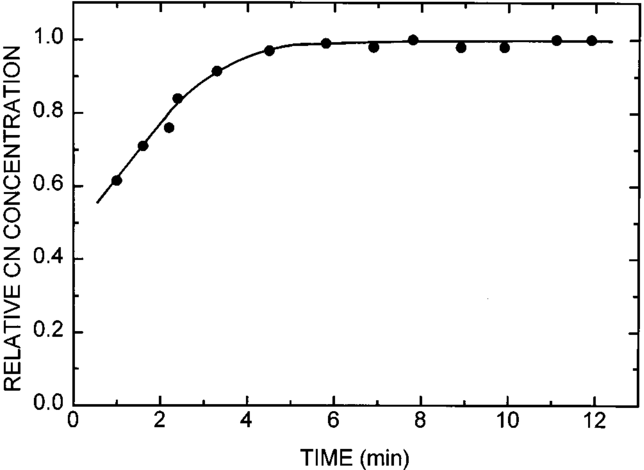

FIG. 6. Relative concentration of the CN species as a function of time in a plasma of 100% N_2 (8.0 sccm) after a 10 min discharge with the following gas flows: 1.5 sccm (C_2H_2) and 6.5 sccm (He).

The latter result is very similar to that depicted in Fig. 5 for the nitrogen plasma and provides further evidence for our previously formulated hypothesis that nitrogen from the nitrogen plasma is incorporated in the polymer film, forming CN units which are subsequently detached from the film surface by the action of the discharge. The nearly constant value of [CN] with time, exhibited by the data of Fig. 6 after about 6 min indicates, in the same manner as the data of Fig. 5 for the nitrogen discharge, that CN units are detached at the same rate as they are formed on the film surface.

IV. CONCLUSIONS

Relative concentrations of the species CH and CN present in glow discharges of mixtures of C_2H_2, N_2, and He were determined by optical emission spectroscopy following the cutting of one of the monomer flows in a "dynamic" form of actinometry. From such studies we have found that both gas phase and surface reactions contribute species to the plasma, thereby influencing its composition. We interpret the experiment in which the decay of [CH] was recorded as a function of time following the interruption of the flow of N_2, as a strong indication that chemical reactions between nitrogen and C_2H_2 molecules contribute significantly to the total rate of generation of the CH species. This contribution to CH apparently dominates those due to fragmentation of C_2H_2 by plasma electrons and to reactions between He^* and C_2H_2.

From the observations in which the concentration of the species CN remained at a relatively high level even though C_2H_2 was absent from the discharge, we concluded that even though gas phase reactions may contribute, reactions on the deposited polymer surface play a significant role in the generation of the CN species. As nitrile functionalities are usu-

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ally present in films deposited from plasmas containing C_2H_2 and N_2, we propose a reaction mechanism model in which, upon interaction with He metastables and other energetic particles from the plasma, the CN species is desorbed from the surface as a consequence of the cleavage of the C–C bond linking the nitrile termination to the surface macromolecules.

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