Comparison of Films Deposited from Pulsed and Continuous Wave Acetonitrile and Acrylonitrile Plasmas

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Continuous wave (CW) and pulsed acetonitrile and acrylonitrile plasmas have been used to deposit thin nitrogen-containing films. Changes in film composition with applied CW power and pulse duty cycle have been monitored using Fourier transform infrared spectroscopy (FTIR) and deposition rates have been measured for both systems. A detailed description of FTIR peak assignments is presented and shows that the composition of films deposited from acetonitrile are insensitive to CW input power and duty cycle. In contrast, acrylonitrile films exhibit a strong compositional dependence on CW input power and duty cycle with the growth of highly conjugated imine and nitrile species. These monomer dependent compositional changes are discussed in terms of their structure, pulse off time durations, and equivalent pulsed and CW applied rf powers. Optical emission spectroscopy (OES) and deposition rate data afford further insight into film formation processes with the two monomers.

KEY WORDS: Pulsed plasma polymerization; acetonitrile; acrylonitrile; Fourier transform infrared spectroscopy; ketene-imine.

1. INTRODUCTION

Plasma polymerization of organic molecules has been extensively studied and is gaining recognition as an important process for the formation of new materials.[1-4] Thin polymeric films with significant nitrogen incorporation, and in particular nitrile groups, exhibit interesting electrical,[5] gas and ion separation,[3] and thermal properties.[6] Generally, plasma polymerization with continuous wave (CW), radio frequency (13.56 MHz) power is used to

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produce these materials, although significant scrambling of the monomer functional groups and UV photon and ion bombardment of the deposited material can occur. Recently, pulsed power has been successfully employed in plasma polymerization of a variety of monomers.[7] Greater retention of the monomer functional group is observed in the resulting polymeric film with pulsed plasma polymerization.[8] One reason for this is that pulsed plasmas provide access to lower CW equivalent powers because the rf power is only on for a portion of the cycle time. Use of pulsed sources also reduces trapped radicals in the film,[9] lowers deposition surface temperatures, decreases high energy ion bombardment and UV flux to the surface, and provides greater control over the resulting film chemistry.

CW plasma polymerization has been used to deposit films from a variety of nitrile containing monomers. Inagaki et al.[10] examined acrylonitrile, 1,2-dicyanoethylene, and tetracyanoethylene. Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) analyses of the resulting films showed that highest retention of nitrile groups occurred using monomers with only one nitrile group and at low (10 W) CW powers. Panchalingam et al.[11] investigated the pulsed plasma polymerization of a variety of monomers including acrylonitrile. They observed an increase in nitrile functionality with a decrease in pulse duty cycle, although they did not investigate other nitrile monomers and their dependence on film properties. Timmons et al.[12] also deposited films from pulsed allyl amine and allyl alcohol and observed significant retention of amine and alcohol functionality with duty cycles of 10% or less. They proposed that deposition occurred through reaction with the vinylic double bond.

This study seeks to provide a critical comparison of CW versus pulsed plasma polymerization of two nitrile-containing monomers: acetonitrile and acrylonitrile. While both of these starting materials, especially acrylonitrile, have been studied extensively in the past, the FTIR peak assignments for the nitrogen-containing functional groups have been repeatedly disputed. This paper presents a complete FTIR analysis of films deposited from CW and pulsed acetonitrile and acrylonitrile plasmas. Optical emission spectroscopy (OES) and deposition rate data afford further insight into film formation processes with the two monomers.

2. EXPERIMENTAL METHODS

All films were deposited in our home-built inductively coupled rf plasma reactor, described previously.[13,14] Input power for CW depositions was varied from 1–100 W, while for the pulsed experiments the applied peak power was kept constant at 300 W. The equivalent CW power can be determined by calculating the time averaged power applied over the entire pulse cycle.

For a 2/13 ms pulse sequence, this corresponds to an equivalent CW power of 40 W and a 2/198 ms pulse sequence corresponds to 3 W. Pulse on time and duty cycle (defined as the ratio of pulse on time to total cycle time) was varied using the internal pulse generator of an RF Power Products RF5S power supply. For each deposition, a freshly pressed FTIR grade KBr (Aldrich) pellet and a silicon wafer (p-type, 110) with 40–60 Å of native oxide were used as substrates. These were placed on glass microscope slides oriented parallel to the gas flow and within the coil region of the plasma reactor. CW and pulsed deposition times ranged from 30 seconds to 15 minutes and for pulsed experiments was defined by the total time the sample was exposed to both pulse on and off cycles.

Acetonitrile (purity greater than 99.9%) and acrylonitrile (purity greater than 99% with hydroquinone monomethyl ether (MEHQ) polymerization inhibitor) were purchased from Aldrich. Acetonitrile was purified through several freeze-pump-thaw cycles. The acrylonitrile was vacuum transferred from the MEHQ polymerization inhibitor, and then degassed with a similar freeze-pump-thaw process. The monomer flow rate was controlled via a Nupro needle valve between the liquid bulb and the reactor. The vacuum lines were left at ambient temperature to reduce polymerization of acrylonitrile. Monomer pressure, monitored with an MKS Baratron capacitance manometer, was allowed to stabilize at 100 mTorr before applying rf power.

The glass reactor as well as the internal glass sleeves were cleaned frequently in a concentrated KOH solution to minimize contamination from previous depositions. After soaking for $\sim$ 12 hours, the glassware was removed and rinsed with de-ionized water. It was then placed in a 200°C oven to dry for several hours before use.

Transmission FTIR spectral analysis on films deposited on KBr pellets and Si wafers was performed ex-situ using a Nicolet Impact 410 FTIR spectrometer (resolution of 8 cm^{-1} and averaging over 100 scans). Spectra shown are corrected for residual carbon dioxide not purged from the FTIR spectrometer (absorbances at $\sim$2340 and 2360 cm^{-1}). Deposition rate and film thickness were determined using a Tencor Alpha Step 100 profilometer using masked Si wafers.

Optical emission spectra (OES) from 240–700 nm were obtained by collecting light through a quartz window situated 10 mm downstream of the coil region. This reactor configuration allows sampling of the plasma emission perpendicular to the gas flow. Emission was imaged onto a 10 μm entrance slit of an Ocean Optics S2000 spectrograph using an optical fiber. The spectrograph was equipped with a 1800 grooves/mm holographic grating and a 2048-element linear CCD-array detector. The emission signal was integrated for 750 ms.

3. RESULTS

3.1. Fourier Transform Infrared Spectroscopy

3.1.1. CW Plasmas

Figure 1 shows FTIR spectra of films deposited from a CW acetonitrile plasma at applied rf powers from 2 to 50 W. Spectra are displayed on the same absorbance scale. All spectra show contributions from hydrocarbon as evidenced by the CH_x stretching vibrations at ~ 2950 cm^{-1} and CH_x bending absorptions at ~ 1400 cm^{-1}.[15] The identification of nitrogen containing moieties is somewhat more difficult because there is some controversy over identification of the absorbance band at 2200 cm^{-1}. Arkovali and Dilsiz[16] assign it as an imine, Li and Netravali[16] as well as Inagaki et al.[15] assign it as a conjugated imine (C=N) stretch, while Barbarossa et al.[17] and Krishnamurthy et al.[18] assign it to a nitrile (C≡N) stretch.

To help identify this peak, FTIR spectra of the acetonitrile and acrylonitrile monomers were obtained on our instrument, Fig. 2. The spectrum for acetonitrile shows a very strong absorbance at 2256 cm^{-1} which can be attributed to the nitrile group. A standard IR spectra of solid polyacrylonitrile[19] is also shown in Fig. 2. This spectra has a very strong nitrile peak at 2245 cm^{-1}. This experimental evidence and the literature support, rules out the nitrile assignment for the absorbance at 2200 cm^{-1}. Since the broad absorbance band at 1630 cm^{-1} is widely accepted as the imine stretch,[3,10] we therefore assign the peak at 2200 cm^{-1} as a conjugated imine. This indicates that the nitrile group of the starting monomer does not remain intact even at the lowest input power (2 W).

In changing from 2–50 W applied rf power, the most notable trends observed in the IR spectra are in the relative peak heights of the conjugated
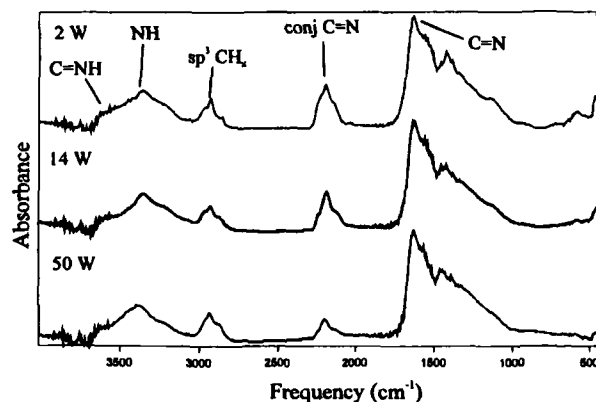

Fig. 1. Transmission FTIR spectra of films deposited from CW acetonitrile plasmas at 50, 14, and 2 W applied rf power.
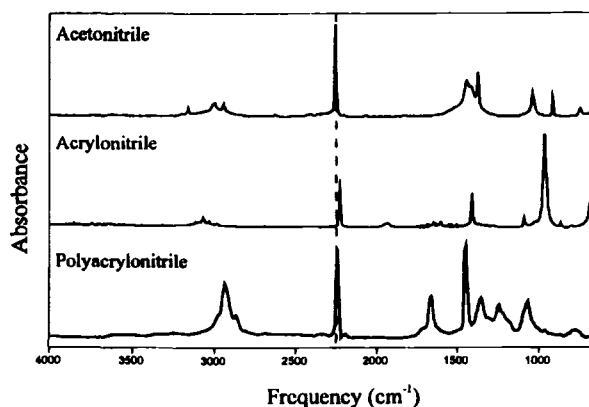
Fig. 2. Transmission FTIR spectra of the acetonitrile and acrylonitrile monomers and a solid polyacrylonitrile standard. FTIR spectra for acetonitrile and acrylonitrile monomers were obtained from a liquid film on NaCl windows at a resolution of 2 cm^{-1} and 100 scans.

imine stretch at 2200 cm^{-1} and nonconjugated imine[3] or C=C stretch at ~1600 cm^{-1}. The relative abundance of the conjugated imine group decreases with respect to the imine/alkene groups at higher input powers (> 14 W). The imine NH stretch at ~3600 cm^{-1}, appearing as a shoulder of the ~3300 cm^{-1} amine peak,[20] also becomes more well defined at higher powers. Nevertheless, the primary or secondary amine absorbance is present in all films studied at all powers and increases in intensity at higher input powers. Absorbances due to sp^3 CH stretching at ~2900 cm^{-1} also increase in magnitude relative to conjugated imine at increased input powers. Although the relative absorbance intensities due to the functional groups may vary, it is clear that the composition of the films deposited from CW acetonitrile plasmas remains constant with input power.

One additional point should be made about these FTIR spectra. In the film deposited from the lowest applied rf power used (2 W) there is a small absorbance peak at 2022 cm^{-1} which we attribute to either a ketene-imine (C=C=N)[10] or an alkyne (C≡C).[3] Panchalingam et al.[11] have attributed this peak to a nitrile group, but with our evidence from standard FTIR spectra of acetonitrile and polyacrylonitrile, Fig. 2, and with the presence of significant amounts of imine groups, the most logical assignment of this peak is a ketene-imine stretching absorption.

Figure 3 contains FTIR spectra for films deposited from CW acrylonitrile plasmas at rf powers from 2 to 52 W. Unlike acetonitrile, films deposited from acrylonitrile show significant compositional differences with input power. At the highest rf power studied, the deposited film contains contributions from NH$_2$ at 3300 cm^{-1}, sp^3 CH stretching at 2950 cm^{-1}, a large complex group of absorptions due to CH and NH bending from 1600 cm^{-1} to 1400 cm^{-1},
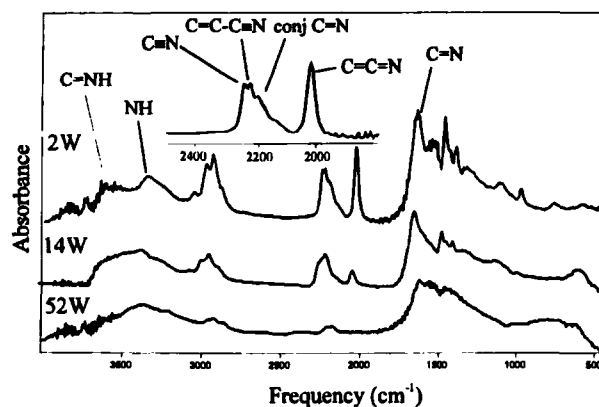
Fig. 3. Transmission FTIR spectra of films deposited from CW acrylonitrile plasmas at 50, 14, and 2 W applied rf power. The inset shows the $1800-2400\ cm^{-1}$ region on an expanded ordinate.

and a small peak at $2200\ cm^{-1}$ that we have attributed to a conjugated imine group. When the applied power is decreased to 14 W, the resulting film has a new absorption at $2022\ cm^{-1}$ due to the presence of a ketene-imine structure (-C=C=N-). This peak is only observed at the lowest powers (2 W) in the acetonitrile system, Fig. 1.

Reducing the power to 2W increases the amount of ketene-imine groups in the film significantly over the other nitrogen containing moieties. There is also a considerable contribution from sp^2 CH stretching at $3050\ cm^{-1}$. On closer examination of the peak at $2200\ cm^{-1}$, we find there is a fine structure of three peaks at $2245\ cm^{-1}$, $2222\ cm^{-1}$, and $2200\ cm^{-1}$, as seen more clearly in the expanded ordinate inset, Fig. 3. These can be assigned as a nitrile (-C≡N),[10] a nitrile conjugated with a double bond (C=C-C≡N), and a conjugated imine (-C=N-),[10] respectively. These assignments match the positions of the conjugated nitrile peak in the acrylonitrile monomer and the nonconjugated nitrile in polyacrylonitirile and acetonitrile, Fig. 2.

3.1.2. Pulsed Plasmas.

Figure 4 shows FTIR spectra of films deposited from pulsed acetonitrile plasmas, using a constant on time of 2 ms and off times from 13 to 198 ms. With all films, there is little variation in film composition with pulse off time and contributions from amine, hydrocarbon and imine groups are observed, Table I. The three spectra shown are for three different time averaged input powers (3, 15, and 40 W) and thus are roughly comparable to the spectra shown in Fig. 1. The relative absorbance intensities for the functional groups in these films exhibit the same trends we observe with films deposited from CW acetonitrile plasmas. Specifically, the intensity of the conjugated imine
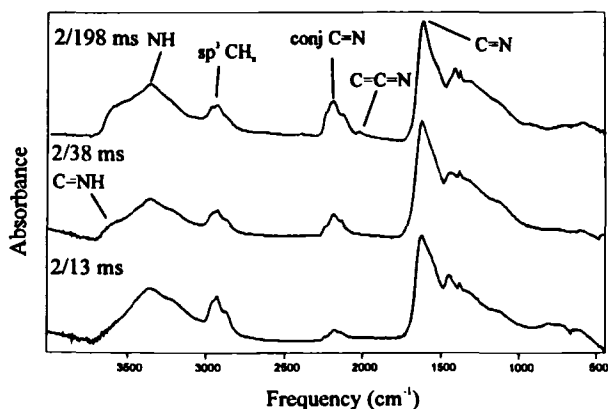
Fig. 4. Transmission FTIR spectra of films deposited from pulsed acetonitrile plasmas with a constant on time of 2 ms and off times of 13, 38, and 198 ms. Peak power is 300 W.

peak at 2200 cm^{-1} increases as the power decreases (lowest average power), and there is a small absorbance band at 2022 cm^{-1} due to the presence of ketene-imine structures. The compositional structure of films deposited from pulsed plasmas are indistinguishable from the structure of films deposited from CW plasmas with similar applied rf powers. Moreover, there are no significant compositional changes with duty cycle. This demonstrates film formation is not dependent on the pulse duty cycle. Note that this is the first monomer we have studied that does not exhibit enhancement of functional group retention with different duty cycles.[8,14]

Table I. Absorbance Band Assignments for Acetonitrile and Acrylonitrile Films

Absorbance (cm^{-1})	Assignment	Reference
1380	CH_3, bend	⎫
1440	CH_2, bend	⎬ 3,10,15
1630	$C=N$	⎭
1642	$C=C$	15
2022	ketene-imine $C=C=N$	11
2200	conjugated $-C=N-$	3, 10, 15
2222	conjugated $C\equiv N$	this work
2245	$C\equiv N$	this work, 10
2850	sp^3—CH_2	⎫
2885	sp^3—CH_3	⎪
2940	CH_2	⎬ 3, 10
2985	CH_3	⎪
3068	sp^2 CH_2	⎭ 10
3350	Primary and secondary N—H	3, 20
3630–3470	C=N—H	10

Figure 5 contains FTIR spectra of films deposited from pulsed acrylonitrile plasmas with a constant on time of 2 ms and a variable off time (13–198 ms). In contrast to the acetonitrile pulsed plasmas, acrylonitrile exhibits a strong dependence on film composition with duty cycle. Films deposited with off times of 13 ms contain significant amounts of primary and secondary amine at 3350 cm^{-1}, sp^3 CH stretching, and alkene/imine stretching at ~1650 cm^{-1}. There is also a small absorbance due to conjugated imine at ~2200 cm^{-1}. At 38 ms off time, the relative intensities of the conjugated nitrile and imine species at 2200 cm^{-1} increase, with the concomitant appearance of the ketene-imine stretch at 2022 cm^{-1} and an imine NH stretch at ~3600 cm^{-1}. Increasing the off time to 198 ms increases the intensities of conjugated C≡N and C=N relative to the C=C/C=N peak at 1650 cm^{-1}, while the intensity of the ketene-imine absorbance peak remains relatively constant.

3.2. Film Deposition Rate

Deposition rates for both CW and pulsed systems are shown in Fig. 6. Rates for films deposited from CW acetonitrile and acrylonitrile plasmas are shown in Fig. 6a. Over the power range studied (2–52 W) acrylonitrile exhibits a higher deposition rate than acetonitrile. Deposition rates for acrylonitrile increase rapidly to 10 W then level off at ~2000 Å/min at higher powers. Acetonitrile plasmas deposit films at much slower rates, although the rate does increase gradually from 15 to 50 W, where it reaches a maximum rate of 700 Å/min.

Deposition rates for pulsed plasma systems are much harder to measure. Because of the varying duty cycle pulsed discharges employ, plotting deposi-
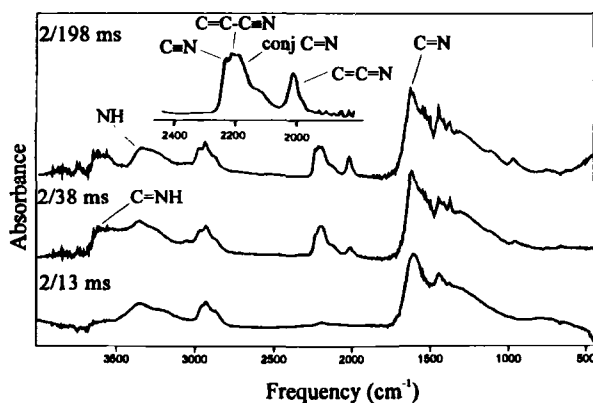

Fig. 5. Transmission FTIR spectra of films deposited from pulsed acrylonitrile plasmas with a constant on time of 2 ms and off times of 13, 38, and 198 ms. Peak power is 300 W. The inset shows the 1800–2400 cm^{-1} region on an expanded ordinate.
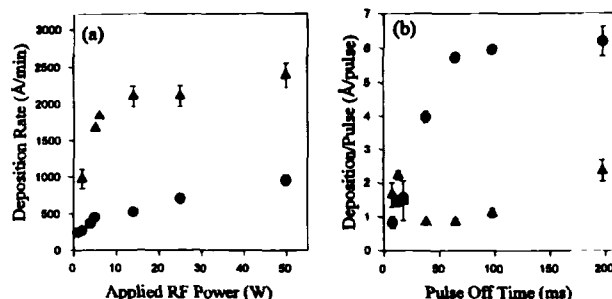
Fig. 6. (a) Deposition rates for CW acetonitrile (closed circles) and acrylonitrile (closed triangles) plasmas as a function of applied rf power; (b) Deposition per pulse for pulsed acetonitrile (closed circles) and acrylonitrile (closed triangles) plasmas as a function of pulse off time.

tion rates per unit time is virtually meaningless. Deposition rates are, therefore, plotted as deposition per pulse vs. pulse off time for depositions carried out at a constant on time of 2 ms and a peak power of 300 W. As seen in Fig. 6b, the deposition rate for acrylonitrile is relatively constant (within experimental error) at $\sim$2 Å/pulse up to $\sim$25 ms off time, decreasing to $\sim$1 Å/pulse at 50 ms off time. At longer off times, there is a small increase in film deposition rate from acrylonitrile pulsed plasmas as the off time increases. This has been observed previously for many other monomers and indicates that film formation processes occur during the off time.[8,11,14,21]

Deposition rates from acetonitrile plasmas exhibit a different behavior with increasing pulse off time. Deposition rates increase rapidly up to $\sim$6 Å/pulse at 50 ms off and then remain constant as the pulse off time increases to 198 ms. This indicates that film formation in acetonitrile plasmas is relatively insensitive to pulse cycle at pulse off time greater than $\sim$50 ms. This type of behavior has only been observed with one other monomer, CH_2Cl_2,[7] and no explanation for the behavior was provided. In our system, we believe that low deposition rates at pulse off times <50 ms are the result of enhanced film ablation, or thermal degradation of the deposited polymer with plasma heating.[22]

3.3. Optical Emission Spectra

To determine the identity of excited state plasma species, optical emission spectra were collected for acetonitrile and acrylonitrile CW plasmas at 50 W. The resulting spectra are shown in Fig. 7 and are very similar for both monomers. The 300–440 nm wavelength range is dominated by emission from the CN violet system.[23] Vibrational bands belonging to the B^2X^+ − $X^2\Sigma^+$ electronic transition of CN can be seen at 330.8 ($\Delta v = +2$), 350.3 ($\Delta v = +1$), 382.7 ($\Delta v = 0$), and 414.9 nm ($\Delta v = +1$)[24] for both acetonitrile
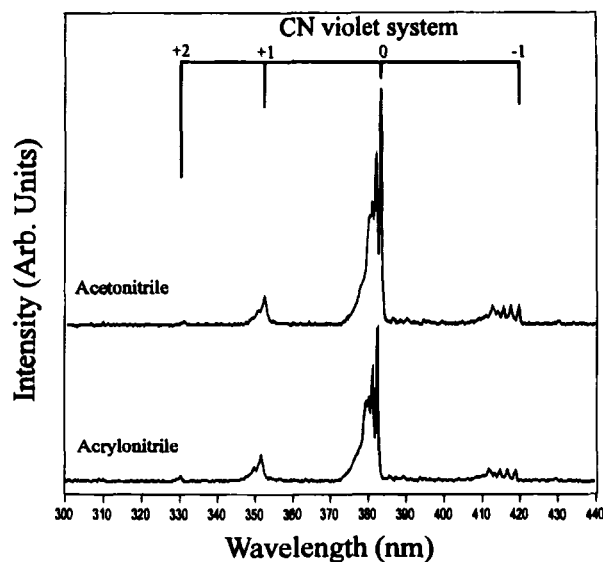
Fig. 7. Time integrated (750 ms) optical emission spectra for 50 W acetonitrile and acrylonitrile CW plasmas. Spectra are shown on the same relative scale.

and acrylonitrile plasmas. The only difference between these two spectra is that CN emission was ~1.5 times more intense in the acetonitrile plasma than the acrylonitrile plasma under identical collection conditions.

4. DISCUSSION

Recently we have conducted several studies of pulsed plasma polymerization of organic starting materials,[8,14,25] as have Timmons and coworkers.[7,11] It is generally believed that with pulsed plasmas, neutral radicals, ions, and high energy electrons are generated during pulse on times and are consumed or quenched during pulse off times.[1] This process can occur at the surface of the growing film or with incoming neutral monomer in the gas phase. This time dependent generation and consumption of gas phase neutral and ionic species can result in a deposition process similar to free radical chain growth polymerization.[20] It is also known that pulsed plasma depositions are extremely monomer dependent.[7] The comparison between acetonitrile and acrylonitrile shown here clearly illustrates this monomer dependence on film properties and in particular functional group retention and control.

Acetonitrile is an unconventional monomer with only one "polymerizable" functional group. [Note: The nitrile group is not a site for conventional polymerization; however, the $C\equiv N$ group is a site of unsaturation. As such,

it can be considered as a polymerizable functional group.] The nitrile carbon is particularly susceptible to attack from nucleophiles[26] and radicals,[27] resulting in film compositions low in nitrile content but high in imine and primary/secondary amine functionality. Formation of amines occurs primarily through reduction with hydrogen which is generated readily from plasmas of organic monomers.[28] Additionally, the OES data show that the primary gas-phase decomposition pathway is C—C bond scission, liberating hydrocarbon and nitrile groups. Comparison of films deposited from CW and pulsed acetonitrile shows that neither the film composition nor deposition rate is strongly dependent on input power (above 10 W) or pulse duty cycle. Moreover, all films contain approximately the same functionality. This implies that film formation proceeds under a similar mechanism in both CW and pulsed systems and that plasma off time relaxation processes do not play a role in the deposition mechanism.

Acrylonitrile is a more complex conventional monomer with two "polymerizable" functional groups: vinyl double bond and nitrile. Both of these groups can form a conjugated π network readily. The effects of this monomer complexity results in the compositional film differences observed with varying CW input power and pulse duty cycle. Inagaki et al.[10] performed a detailed analysis of films deposited from CW acrylonitrile plasmas from 10 to 50 W. Our CW results agree very closely with this previous study. In both studies, an increase in nitrile, conjugated imine, and ketene-imine functionality with a decrease in plasma power is observed.

The formation of ketene-imine groups from the acrylonitrile monomer is believed to result from transformation of film nitrile groups through bombardment by ions or UV irradiation and thus, is indicative of plasma damage to the film.[10] This can be monitored by comparing the ratio of peak areas for the ketene-imine (2022 cm^{-1}) to other CN moieties (2245–2200 cm^{-1}). For the film deposited in the acrylonitrile CW plasma at 2 W, this ratio is ~1:1.6. For comparison, the ratio of peak areas is 1:3.9 for the 2/198 pulsed acrylonitrile plasma, indicating there is significantly more nitrile than ketene-imine in this film. The difference in these ratios between the CW and pulsed plasmas highlights the effect of reducing ion and UV interactions with the depositing films in pulsed plasmas.

Films deposited from acrylonitrile also have conjugate imine structures which are likely formed through a more complicated process. Gas phase radical attack can occur at both the vinylic carbon and the nitrile group. Using conventional polymerization, Liepens and Campbell[27] observed that radicals preferentially attack the nitrile carbon, and not double bonds. Such a process may be responsible for the extended imine conjugation observed here at all CW powers studied. The observation of gas-phase CN radicals in a 50 W acrylonitrile plasma, Fig. 7, indicates that at higher rf powers, cleavage

of nitrile groups in the gas phase can occur. Alternatively, the gas-phase CN radicals could be formed through surface sputtering of the depositing film.[29] This latter process would effectively reduce the nitrile content in the film, limiting possible ketene-imine formation reactions.

Comparison of films deposited from pulsed and CW acrylonitrile plasmas shows that film composition is nearly identical at the highest rf powers. At lower equivalent rf powers, however, films deposited from pulsed and CW plasmas exhibit significant compositional differences. One possible explanation for this is that in the pulsed plasma, chain growth polymerization can occur during the pulse off time. This polymerization mechanism can be very selective and may occur predominantly through the C=C bond, minimizing film rearrangements during deposition. Evidence for this is shown in the absence of sp^2 CH at 3050 cm^{-1} in films deposited from pulsed plasmas. Moreover, the observed increase in deposition rate at long off times also implies that film formation occurs during the off times.[21] In contrast, films deposited using CW plasmas have significant retention of the vinylic group as indicated by the persistence of sp^2 hybridized CH. These data show that during pulsed plasma polymerization, greater retention of the nitrile functional group is possible due to the chain growth polymerization during pulse off times.

5. CONCLUSIONS

Using acetonitrile and acrylonitrile monomers, we have deposited thin nitrogen-containing films from both pulsed and CW plasmas. With acetonitrile, film composition does not change appreciably by varying applied rf power or duty cycle. This is in sharp contrast to the level of control over film chemistry we have achieved with pulsed plasma polymerization of other monomers. Films deposited from the more complex monomer acrylonitrile, however, do exhibit functional group changes with both applied power in CW plasmas and duty cycle in pulsed plasmas. This work demonstrates that careful and thoughtful selection of starting materials for pulsed plasma polymerization can result in effective molecular tailoring of materials. Synthesis of monomers that enhance our ability to predict film composition is the next step in the control and design of new materials.

REFERENCES

1. H. Yasuda, *Plasma Polymerization*, Academic Press, Orlando, (1985).
2. H. Yasuda, M. O. Bumgarner, and J. J. Hillman, *J. Appl. Polym. Sci.* 19, 1403 (1975).
3. T. A. Bell, T. Wydeven, and C. C. Johnson, *J. Appl. Polym. Sci.* 19, 1911 (1975).
4. H. Yasuda and T. Hsu, *J. Polym. Sci.* 15, 81 (1977).
5. A. H. Bhuiyan, N. R. Rajopadhye, and S. V. Bhoraskar, *Thin Solid Films* 161, 187 (1988).
6. A. Kubono, H. Higuchi, S. Umemoto, and N. Okui, *Thin Solid Films* 229, 133 (1993).
7. V. Panchilangam, X. Chen, C. R. Savage, R. B. Timmons, and R. C. Eberhart, *J. Appl. Polym. Sci. Polym. Symp.* 54, 123 (1994).
8. N. M. Mackie, D. G. Castner, and E. R. Fisher, *Langmuir* 14, 1227 (1998).
9. P. M. McCurdy, J. Truitt, and E. R. Fisher, *J. Electrochem. Soc.* 145, 3271 (1998).
10. N. Inagaki, S. Tasaka, and Y. Yamada, *J. Polym. Sci. Polym. Chem.* 30, 2003 (1992).
11. V. Panchalingam, X. Chen, H-H. Huo, C. R. Savage, R. B. Timmons, and R. C. Eberhart, *ASAIO J.* 39, M305 (1993).
12. C. L. Rinsch, X. Chen, V. Panchalingam, R. C. Eberhart, J-H. Wang, and R. B. Timmons, *Langmuir* 12, 2995 (1996).
13. K. H. A. Bogart, N. F. Dalleska, G. R. Bogart, and E. R. Fisher, *J. Vac. Sci. Technol. A* 13, 476 (1995).
14. N. M. Mackie, N. F. Dalleska, D. G. Castner, and E. R. Fisher, *Chem. Mater.* 9, 349 (1997).
15. Z-F. Li and A. N. Netravali, *J. Appl. Polym. Sci.* 44, 319 (1992).
16. G. Arkovali and N. Dilsiz, *Polym. Eng. Sci.* 30, 485 (1990).
17. V. Barbarossa, S. Contarini, and A. Zanobi, *J. Appl. Polym. Sci.* 44, 1951 (1992).
18. V. Krishnamurthy, I. L. Kamel, and Y. Wei, *J. Polym. Sci. Polym. Chem.* 27, 1211 (1989).
19. D. O. Hummel, *Infrared Spectra of Polymers in the Medium and Long Wavelength Regions*, Interscience, New York (1966).
20. H. Yasuda, M. O. Bumgarner, H. C. Marsh, and N. Morosoff, *J. Polymer Sci. Polym. Chem.* 14, 195 (1976).
21. C. R. Savage, R. B. Timmons, and J. W. Lin, *Structure-Property Relations in Polymers*, Advances in Chemistry Series 236, American Chemical Society, Washington, D.C., p. 745, (1993).
22. A. E. Lefohn, N. M. Mackie, and E. R. Fisher, unpublished results.
23. E. Aldea, A. P. Caricato, G. Dinescu, A. Luches, and A. Perrone, *Jpn. J. Appl. Phys.* 36, 4686 (1997).
24. S. F. Durrant, E. C. Rangel, and M. A. Bica de Moraes, *J. Vac. Sci. Technol. A* 13, 1901 (1995).
25. M. A. Leich, N. M. Mackie, K. L. Williams, and E. R. Fisher, *Macromolecules* 31, 7618 (1998).
26. E. M. Fettes, *Chemical Reactions of Polymers*, Interscience, New York, (1964).
27. R. Liepins, D. Campbell, and C. Walker, *J. Polym Sci.: Polym. Chem.* 6, 3059 (1986).
28. H. Yasuda, M. O. Bumgarmer, and J. J. Hillman, *J. Appl. Polym. Sci.* 19, 531 (1975).
29. S. F. Durrant, E. C. Rangel, and M. A B. de Moraes, *J. Vac. Sci. Technol. A* 13, 1901 (1995).