Plasma Polymerization of Allylamine/ 3-Aminopropyltriethoxysilane Mixtures: Surface Nitrogen Control

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SYNOPSIS

A study has been conducted to determine the effects of gas-feed composition and RF power on the deposition rate and on the surface nitrogen content of thin films produced by plasma polymerization of allylamine/3-amino-propyltriethoxysilane (AA/3-APTS) mixtures. It has been found that while the deposition rate decreases slightly by increasing the AA content in the mixture, the surface nitrogen content, determined by XPS as N : Si molar ratios, increases up to a value of 8 : 1. Moreover, the nitrogen increase is not linear with the AA concentration and a maximum in the N/Si values is found for AA/APTS ratios close to 3 : 1, at all RF powers. The discussion on the polymerization mechanism for the mixture is based on evaluating and combining the behavior of each component, when plasma-polymerized alone in similar conditions.

INTRODUCTION

In the field of thin film deposition using RF and MW discharges, plasma polymerization of siloxanes and silazanes is fully described in the literature.[1-5] Plasma deposition of aminosilanes has been used in our laboratories in order to obtain films which strongly adhere to SiO substrates, are homogenous, and have controlled thicknesses. The plasma-enhanced reaction, which involves decomposition and polymerization, produces a film which contains nitrogen bonded to carbon by single, double, and even triple bonds.

The aim of this work is to study the possibility of increasing the surface nitrogen content by adding allylamine to the gas feed, without altering the adhesion properties of the film. XPS and IR spectroscopies have been used to characterize surface and bulk compositions, by comparing nitrogen and silicon relative concentrations. Although XPS results are easily quantified by measuring peak areas, the IR peaks of these films are broad and not accurately measurable. Therefore, the XPS data were used for quantitative and the IR for qualitative information.

EXPERIMENTAL

The deposition system is schematically shown in Figure 1. Stainless steel parallel plate electrodes, positioned at a distance of 2.5 cm, are contained in a mechanically pumped pyrex reactor. Plasma excitation was produced by using a 2 MHz RF generator at powers varying between 20 and 100 W.

The gas feed was produced by bubbling the mass flow controlled carrier gas in separate monomer reservoirs. By appropriately varying the temperature of the reservoirs and the apertures of the needle valves, it was possible to obtain Allylamine to APTS molar ratios varying between 0 and 8. Total gas flow and pressure in the reactor were kept constant in all experiments at 20 sccm and 100 Pa, respectively. The polymer films were deposited on Si substrates and film thicknesses were measured by using a profilometer (Alpha-Step 200 Tencor). Sample surfaces were analyzed with an optical microscope to insure that silicon oxide substrates were completely covered

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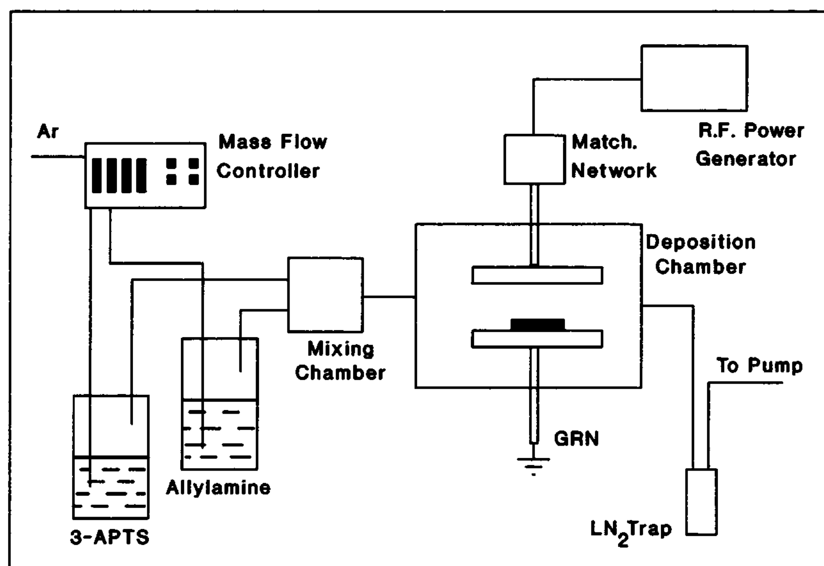

Figure 1 Schematic of experimental apparatus for plasma polymerization.

by the film, prior to XPS testing. XPS measurements were performed with a VG Escalab MkII spectrometer using Al Kα as an excitation source at 1486.6 eV. Peaks arising from the ls emission of carbon, oxygen, nitrogen, and the 2p emission of silicon were recorded with a VGS 5000 data system and subsequently quantified using Scofield normalization factors.[6] Nitrogen levels are reported as N ls/Si 2p ratios in order to normalize instrumental errors and variations induced by surface contamination. Infrared spectra were obtained with a Bruker IFS 88 spectrometer and relevant software. Adequate signal to noise ratios were reached after 500 scans. Silicon was used as reference.

RESULTS

All samples grown following the experimental conditions described above, exhibit good adhesion properties on the Si substrate. On the other hand, plasma polymerization of pure AA produces weakly adhesive films. Therefore, the range of allylamine concentration investigated represents a compromise for obtaining a high nitrogen containing film which still show good polymer/substrate adhesion.

The data reported in this article compare films grown by adding increasing amounts of allylamine in the gas mixture, to films grown from pure 3-APTS. Literature data are used for the composition of pure allylamine films.[7]

Deposition Rate

Film thicknesses, measured on more than 30 samples, are a function of the deposition parameters and vary between 150 and 1500 nm. The dependence of the deposition rate with power for the mixtures follows the trend of pure 3-APTS, in that it increases with RF power. In Figure 2, the deposition rates at 20, 70, and 100 W are plotted vs. AA/APTS ratios, which range from 0 to 8 in the gas feed. The effect of AA on the deposition rates seems to be similar at all powers as can be seen in Figure 3, where the rates are normalized to their maximum Rd values.

XPS Measurements

The widescan spectrum of a typical film grown at 100 W and at an AA/APTS ratio of 3.2 is shown in the upper portion of Figure 4. The lower portion represents the high resolution spectra of C ls, N ls, O ls, and Si 2p photoelectrons from the same sample, normalized to the same height. Upon varying the deposition parameters, all samples exhibit similar binding energies but different intensity ratios.

Binding energies, taken at the peak maximum and band widths, taken at the full width at half-maximum, are reported in Table I. The BE assignments are in agreement with literature data[8] for Si—O, C—C—H, and C—C—N species. The latter is probably present in more than one form, causing the broadening of the N ls peak. The C ls region exhibits a broad unresolved structure which appears asymmetric on the high BE side. This band

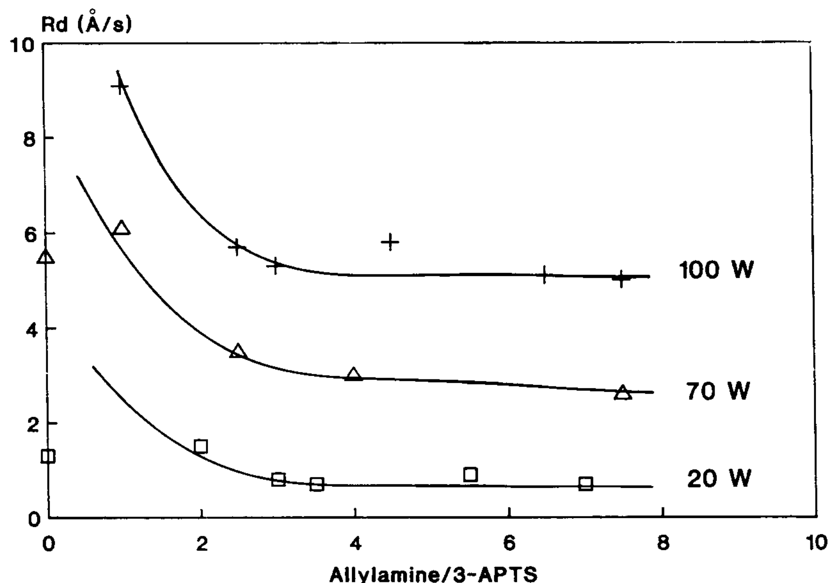

Figure 2 Deposition rates in A/s plotted vs. AA/APTS at different RF powers.

is generated by the sum of overlapping aliphatic, aminic, and oxidized (C—O) peaks, which cannot be accurately identified. C—O species are assumed to be present in low concentration because of the low peak intensity near 288.0 eV.

Therefore, emphasis is placed on the quantitative elemental changes of nitrogen, which occur using different deposition parameters. In order to minimize the instrumental error (surface atmospheric contaminations, X-ray flux fluctuations), the N level is measured relative to the Si 2p intensity.

In Figure 5 the N/Si values are plotted vs. RF power at three different AA/APTS ratios. The advantage of adding allylamine to the mixture, for obtaining higher N content, is evident. While the N/Si ratio, in agreement with other authors,[9] is lower than unity in films of polymerized pure 3-APTS, by adding allylamine, the N/Si ratio increases up to a maximum value of 8. It is interesting to note that this increase is not linear with the AA concentration. In fact, as shown by the plots of N content versus AA/3-APTS at various powers in Figure 6, the

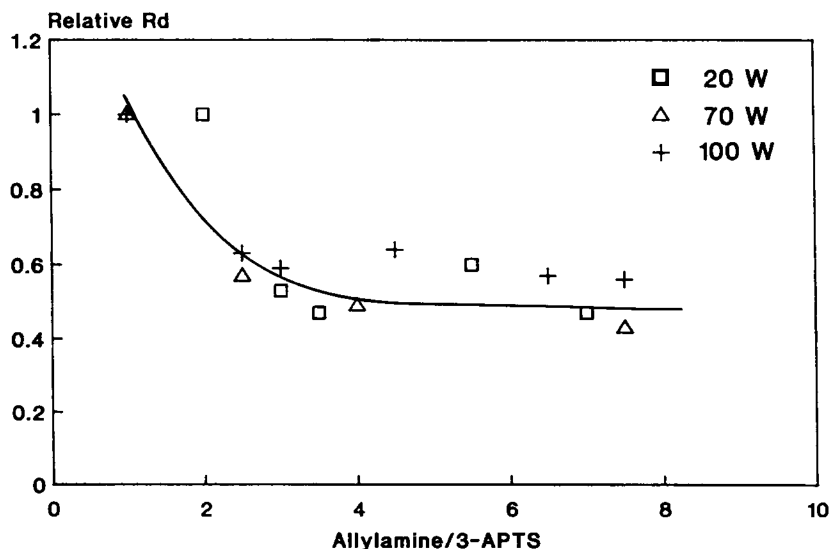

Figure 3 Relative deposition rates vs. AA/APTS. These are obtained by normalizing the data from Figure 2 to their highest value, in each curve.

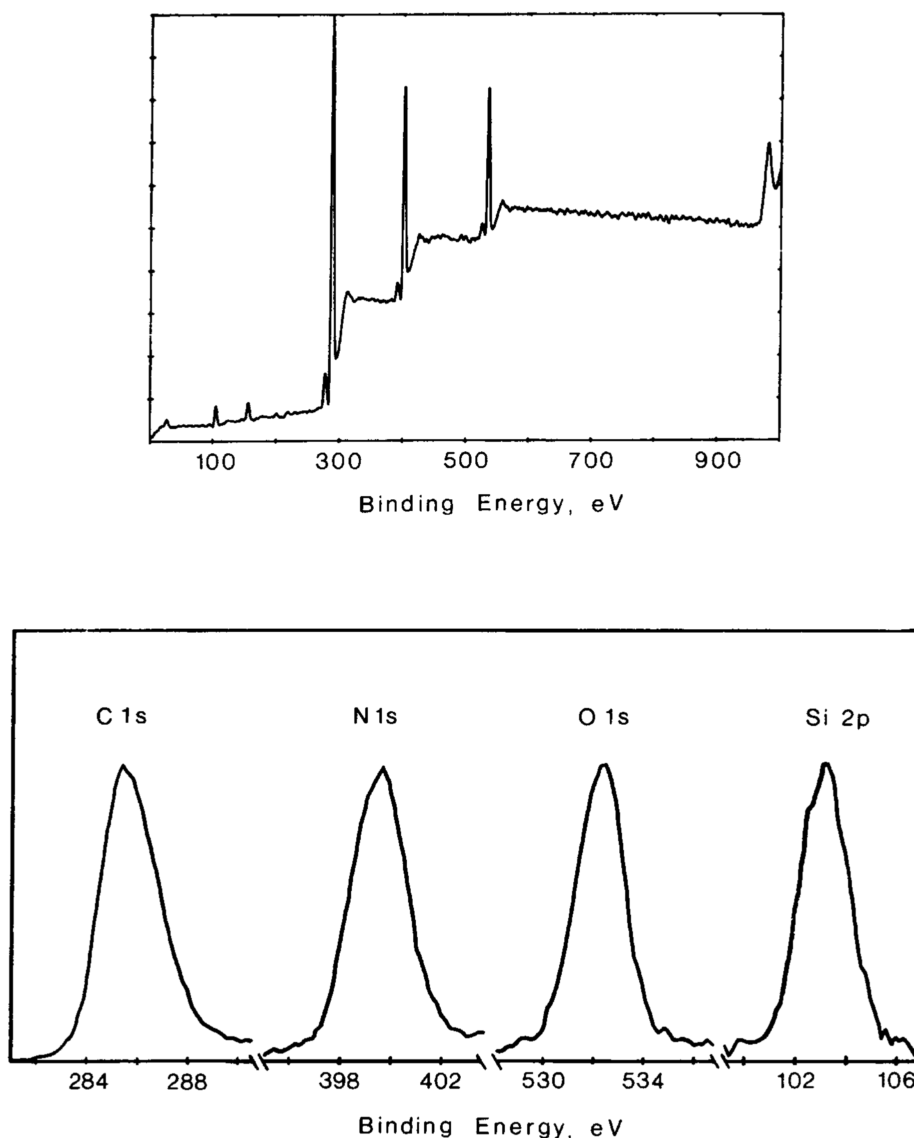

Figure 4 XPS spectra of one representative sample: AA/APTS = 3.2, 100 W. Upper: widescan 0–1000 eV; analyzer set at 100 eV pass energy. Lower: narrow scans of C ls, N ls, 0 ls, and Si 2p regions; analyzer set at 20 eV pass energy.

Table I Binding Energy and FWHM Values Averaged for All Samples with a Variation of ±0.2 eV

Element	BE	FWHM
C ls	285.6	2.8
N ls	399.4	2.4
O ls	532.4	2.0
Si 2p	103.2[a]	2.0

[a] This value is taken as reference for electrostatic charging shifts.

maximum nitrogen intensity is found for a gas mixture ratio near 3 : 1. Above this value, the nitrogen level remains high at high power (70–100 W), while it decreases at low power (20–40 W).

FTIR Measurements

Infrared spectroscopy was used for bulk characterization of the polymeric films. For qualitative identification of aliphatic and aminic moieties the IR data yield more information than the XPS data, although Si—O species are clearly detected by both

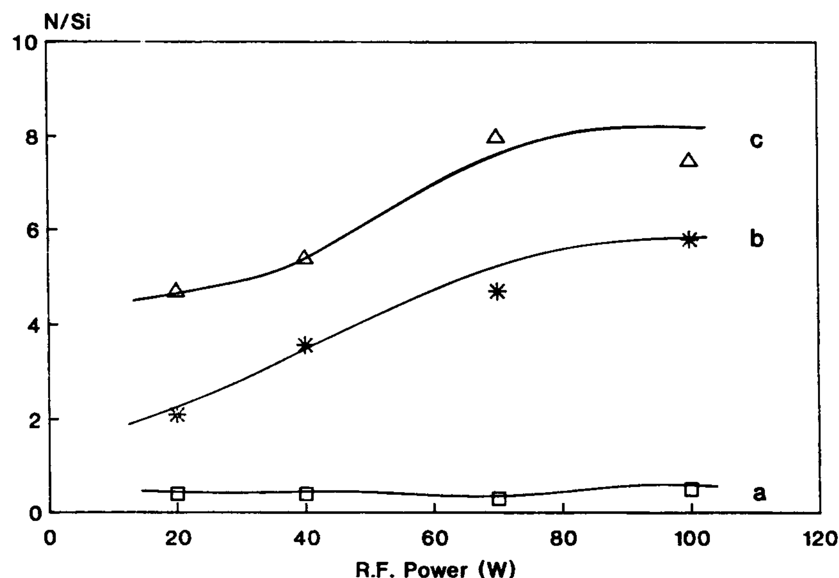

Figure 5 XPS N ls/Si 2p atomic concentration ratios plotted vs. RF power at different AA/APTS ratios: (a) 0; (b) 7; (c) 3.

techniques. Quantitatively, a computation of the IR data was not attempted because of the background unlinearity and also because of the large width of the N-species bands. In Figure 7, IR spectra of four AA containing samples are shown in addition to the spectrum of plasma-polymerized 3-APTS alone. The peak assignments are reported in Table II. The spectra of AA/APTS films show higher intensity bands related to N-containing species than the film of APTS alone, in the regions of 3300, 2200, and 1600 cm^{-1}. These peaks are assigned to N—H stretching, C—N stretching, and N—H bending plus C—N stretching, respectively.[5,7,9] The absence of a sharp peak at 3030 cm^{-1} indicates that no C—C double bonds are present in the films.

The spectra of Figure 7 show that the intensity of the band at 1600 cm^{-1} (N-containing species), relative to the band at 1100 cm^{-1} (Si-containing

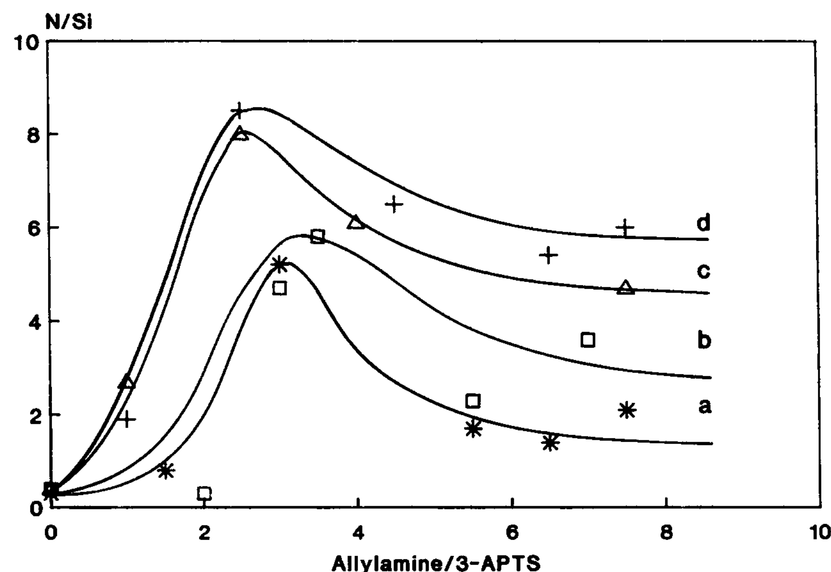

Figure 6 XPS N ls/Si 2p atomic concentration ratios plotted vs. AA/APTS ratios at different RF powers: (a) 20 W; (b) 40 W; (c) 70 W; (d) 100 W.

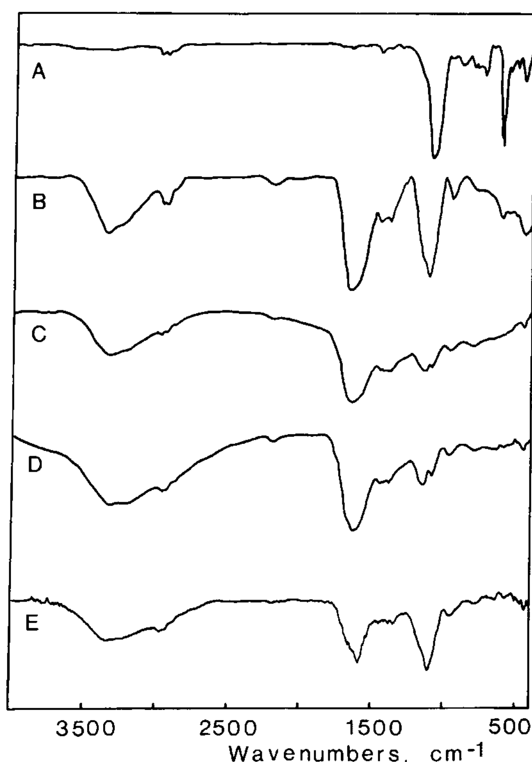

Figure 7 FTIR spectra of films deposited with the following AA/APTS ratios and RF powers: (A) 3-APTS only; 70 W; (B, C, D) AA/APTS = 1.1, 2.8, 6.5; 100 W; (E) AA/APTS = 6.3; 40 W.

species), is a function of the deposition parameters, as found also in the respective XPS N/Si values of the same samples.

DISCUSSION

The uncertainty in the IR quantification does not allow an accurate determination of possible differences between surface and bulk composition of the films. Nevertheless, the general agreement between the IR spectra shown in Figure 7 and the respective XPS data indicates that these differences are small. Similar qualitative correlation for XPS and IR data was found in Ref. 5.

Therefore, we believe that XPS nitrogen to silicon ratios are sufficiently representative of the bulk situation and can be used to evaluate a growth mechanism. In order to understand the plasma behavior of the gas mixture, it is convenient to analyze first the polymerization mechanism of each component when present alone in a glow discharge. Earlier studies on the plasma polymerization of allylamine, carried out by Bell et al.,[7] show that the nitrogen to carbon ratio is almost completely retained in the bulk polymer. Polymerization occurs through a complex variety of reactions involving free radicals, which finally bring to saturation of the allylamine C — C double bond and formation of mainly double-bonded and partially single- and triple-bonded carbon nitrogen species.

On the other hand, plasma polymerization of 3-APTS is not as well documented in the literature, although studies on similar siloxanes are available.[9] Tajima and Yamamoto[4] have found that plasma polymerization of hexamethyldisiloxane occurs by oxidation of the Si atoms and formation of an Si — O — Si network, containing variable amounts of Si — C and Si — O species.

Our findings are in general agreement with these results, although the combination of two components results in additional complexity. The addition of AA to 3-APTS, although very effective for the purpose of increasing nitrogen in the films as seen in Figure 5, opens some questions regarding the behaviour shown by Figure 6. The line shape of the N/Si plots indicates that the AA concentration in the gas feed is not the only parameter determining the N level in the films. In fact, this alone cannot explain the reason for the maximum found at AA/3-APTS ratios equal to 3 and for N/Si ratios ranging from less than one to a maximum of about 8.

A possible explanation lies in the different plasma behavior of each component. We have observed that 3-APTS polymerizes more rapidly than allylamine. In fact, although a good discharge was obtained for 3-APTS at 20W nonimal power in our reactor, it was not possible to sustain a glow discharge with pure allylamine at this power. Therefore, for high AA content in the mixture, at low power, polymerization occurs mainly at the expenses of the siloxane,

Table II Frequencies and IR Band Assignments for Plasma-Polymerized Films

Frequency (cm^{-1})	Assignments[a]
3330–3340	ν as(NH_2)
3200	ν s(NH_2)
2960	ν as(CH_3)
2940	ν as(CH_2)
2880	ν s(CH_3), ν s(CH_2)
2190	ν (CN)
1600	δ (NH_2)
1380	δ (CH_3)
1000–1100	ν (SiOC), ν (SiOSi)

[a] ν = stretching; δ = bending.

and the N content is low, similar to the one measured for pure 3-APTS [see Figs. 6(a) and 6(b)].

At high power and high AA concentration (AA/3-APTS = 6), the N content is high because in this case, polymerization effectively occurs also by saturation of the C—C bond of allylamine. This produces a polymeric chain containing alternating Si—O—Si and C—C—N= groups whose relative concentrations are also a function of the AA content in the mixture. However, it is important to note that these are not the conditions for obtaining the maximum N/Si level in the film. This maximum is found at an AA/3-APTS ratio equal to 3 ± 0.5. Because polymerization of 3-APTS occurs mainly through breakage of ethyl—O—Si bonds, it seems that at this ratio the siloxane group has the highest probability to react with aminoallylic radicals, rather than with another siloxane group. Below the maximum, the limiting factor is the AA concentration. The N level increases in the films up to the AA/3-APTS ratio of 3, which is the number of ethoxy groups bonded to Si in the monomer.

Above this value the limiting factor is the lower reactivity of AA relative to 3-APTS. Therefore, even at 100 W and for large amounts of allylamine, the siloxane still polymerizes faster and the N/Si ratio decreases. Such a mechanism is in agreement with the fact that the deposition rate decreases at all powers by adding AA up to a 3 : 1 ratio in the mixture, after which it remains more or less constant.

Further experiments are needed to verify these hypothesis. One possible verification, which will be undergone in the near future, is to repeat the set of depositions, using siloxane monomers with a different number of ethoxy groups and see if the line shape of the N/Si vs. AA concentration curves are changed accordingly.

CONCLUSIONS

The experiments carried out in this work indicate that the addition of allylamine is an effective way to increase the nitrogen content of plasma-polymerized 3-APTS films. The deposition rate increases with RF power while it decreases with AA concentration up to the AA/3-APTS ratio equal to 3 : 1, after which it remains constant.

The AA/3-APTS ratio equal to 3 seems to play an important role in the polymerization mechanism because there is evidence for a maximum in the XPS N/Si ratios. In order to explain such behaviour, two mechanisms can be hypothesized: before the maximum, the polymerization is controlled by the AA concentration; after the maximum, the main controlling parameter is the power transferred to the mixture.

Further studies will be undergone on siloxanes containing different number of alkhoxy groups to verify these hypotheses.

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