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The growth and chemical structure of thin photonic films formed from plasma copolymerization. Part II. Effect of monomer feed location

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Abstract

Plasma copolymerization of benzene and octafluorocyclobutane (OFCB) has been successfully applied in the fabrication of photonic films with controllable refractive index profiles by accurately adjusting the comonomer feed ratio and feed locations during plasma enhanced chemical vapor deposition (PECVD). XPS, IR, and spectroscopic ellipsometry were used to determine the deposition rate, chemical composition/structure, and optical properties of the PECVD films. Three different feed locations were chosen for the OFCB monomer including downstream from the plasma zone (DS), the plasma zone edge (PE), and the center of the plasma zone (PZ). The benzene was always fed in at the DS position. For both plasma homo- and copolymerization, film deposition rates were highest utilizing the PZ feed. The addition of small amounts of benzene increased these deposition rates substantially, but also led to a dramatic decrease in the F/C ratio and significant variations in different structural units ($CF_{x(x=1-3)}$) indicating the complex subtleties of plasma copolymerization. The refractive indices of the polymer thin films scaled linearly with the F/C values determined from the film composition studies.

Keywords: PECVD; Plasma copolymerization; Polymer photonics.

1. Introduction

Plasma copolymerization is a relatively new method for the synthesis of polymer materials as compared to plasma homopolymerization [1]. Although plasma polymerization has received significant attention in the last 20 years, the majority of this interest has focused on plasma homopolymerization using single monomer feed streams [2–5]. Only limited reports on the mechanism of plasma copolymerization have been published due to the complicated plasma environment [6–13]. In plasma copolymerization, the initiation reactions are based on the collision probability between monomers and the excited species. These reactions can be instantaneous, or stepwise, depending on the reactivity of the selected comonomers and the plasma process conditions [1,12,14–16]. The appeal of plasma copolymerization is the much larger palette of chemical and optical functionalities offered by mixed monomer chemistry, particularly those not obtainable by conventional wet-chemistry [17–25]. A combination of properties not available using single monomer sources can be accessed as has been demonstrated recently [26,27] in the fabrication of several complex polymeric photonic thin film structures. By adjusting the comonomer (benzene and octafluorocyclobutane) feed ratio and feed location, photonic films/coatings with optical thickness control on the nanometer scale were fabricated with a controllable refractive index profile [27].

This paper is a continuation of this work [27,28] concentrating on the chemistry and mechanism of plasma copolymerization using benzene and OFCB as comonomers. In the work reported here, three different OFCB feed locations were selected: downstream from the plasma zone (DS), at the plasma zone edge (PE), and at the plasma zone center (PZ). The effect of these feed locations on the deposition rate, possible copolymerization mechanisms, and chemical composition/structure of the PECVD films are discussed in detail. Furthermore, the relationship between refractive index (RI) and the film composition/structure is obtained.

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2. Experimental procedures

The flowing afterglow reaction system used for plasma homo-/copolymerization is essentially the same as described previously [26,27]. Octafluorocyclobutane (OFCB, C_4F_8) compressed gas (SynQuest Laboratories, Inc., with a purity of $>99\%$) was used as one of the comonomers (as the low refractive index component) and its flow rate was controlled by a Sierra 902C flow-controller, in the range of 0.5–3 cm^3/min. The vapor of HPLC grade (99.9%) benzene (C_6H_6, Aldrich Co.) was used as the other comonomer (as the high refractive index component) and its vapor flow rate was controlled by a manually adjusted high-accuracy metering-valve, in the range of 0.004–0.3 cm^3/min. Both monomers were used as received without any further purification. Three feed locations for the OFCB monomer were chosen for this study including the center of the plasma zone between the two parallel plate electrodes (PZ), the edge of the plasma zone, ~3 cm downstream away from the plasma zone center (PE), and 10 cm downstream from the plasma zone center (DS). Benzene was always fed in at the DS location and the substrates for film deposition were placed approximately 1.5 cm further downstream from the monomer (DS) inlet. Fig. 1 is a schematic of the feed locations of both comonomers.

The comonomer feed ratio was expressed by $b/(b+f)$, where b denotes the benzene volume flow rate (cm^3/min) and f, the OFCB volume flow rate (cm^3/min). The higher fluorine/carbon (F/C) ratio films were obtained by maintaining a constant OFCB volume feed rate (3 cm^3/min) while gradually adding a small amount of benzene (from 0 to 0.18 cm^3/min). The lower F/C ratio films were obtained by maintaining a constant (comparatively high) benzene volume flow rate (0.18 cm^3/min) while decreasing the OFCB flow rate (from 3 to 0 cm^3/min). Table 1 lists the 11 plasma homo-/copolymerized films used to study the effects of the monomer feed location.

Plasma homo-/copolymerized films were deposited directly on potassium bromide (KBr) disks for FTIR analysis, which was performed on a Perkin–Elmer Spectrum 2000 FT-IR spectrometer in the transmission mode, with a scanning range of 400–4000/cm in 1/cm increments. The XPS analysis was carried out in a Surface Science Instruments M-Probe using monochromatic Al K_α X-rays (energy 1487 eV), and the films were deposited on Si substrates. The surface composition and fluorine to carbon atomic ratios were measured from survey scans taken with an analyzer pass energy of 150 eV (corresponding to an energy resolution of about 1.5 eV). Measurements were also taken of the C 1s line-shape at a pass energy of 100 eV (higher energy resolution) in order to distinguish the different carbon chemistries in the films. A low energy electron flood source was used to reduce and stabilize electrical charging during analysis. The detailed procedure for the XPS measurement was reported elsewhere [28]. The ellipsometry measurements were carried out with a Woollam variable-angle spectroscopic ellipsometer system, and the detailed procedure was also reported elsewhere [26].

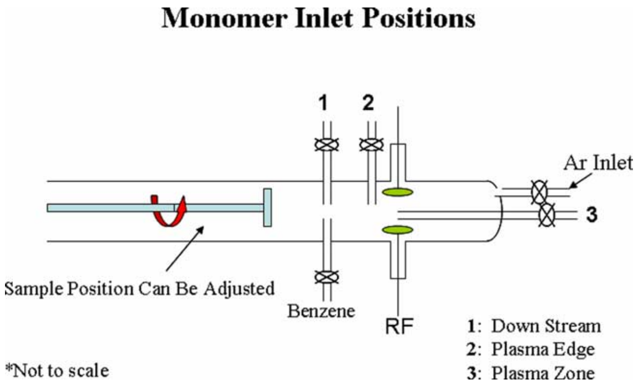

Fig. 1. Schematic of PECVD deposition apparatus with three different OFCB feed locations marked, plasma zone center (PZ), plasma zone edge (PE), and down stream area (DS).

3. Results and discussion

As described in previous papers [26–28], plasma homo-/copolymerized photonic films have been successfully deposited. The refractive index was manipulated to the second decimal place by controlling the fluorine/carbon atomic ratio (F/C) of the resultant films by manipulating the comonomer volume feed ratio, $b/(b+f)$, via accurate control of the benzene and OFCB feed rates [28], and by changing the OFCB feed location from downstream to the center of the plasma zone [27]. The primary reason for these two modifications was the reactivity differences between the two monomers as understood based on the initiation mechanism of collision mediated energy transfer [9] during plasma polymerization. In this work, the effects of OFCB monomer feed location are discussed in detail.

Changing the OFCB location from DS to PE to PZ increased the film deposition rate substantially, from 1.4 to 2.7 to 3.3 nm/min, respectively, for homopolymerized films. The initiation of plasma polymerization is dependent on the collision mediated energy transfer in the gas phase. When an excited species with high energy collides with a monomer, it transfers part, if not all of its energy to activate the monomer. In the PZ location, there are many high-energy species formed, including ions, electrons, radicals, metastable and excited molecules. The large number of excited species and their high energy (>20 eV) greatly increase the probability of OFCB bond dissociation via the opening of the ring structure and defluorination. This is contrasted to conditions in the DS location where only metastable argon (~12.5 eV) is available as the initiator due to the very short lifetimes of the high-energy species [9,26,29–31]. Hence, by feeding OFCB molecules into the PZ location, large concentrations of activated fluorine species are formed as compared to the DS location, resulting in a high deposition rate.

Table 1

Monomer feed volume rates and ratios during the plasma homo-/copolymerization, and the fluorine/carbon atomic ratios of the resultant films determined by XPS for the three feed locations of OFCB: (1) plasma zone center (PZ); (2) plasma zone edge (PE); and (3) down stream (DS)

Sample name	OFCB feed rate (cm^3/min)	Benzene feed rate (cm^3/min)	Monomer feed ratio ($b/(b+f)$)	F/C atomic ratio (PZ)	F/C atomic ratio (PE)	F/C atomic ratio (DS)
Homopolymer film of benzene	0	0.18	1	0	0	0
Copolymer film BF9	1	0.18	0.15	0.23	0.23	0.09
Copolymer film BF8	2	0.18	0.081	0.36	0.32	0.12
Copolymer film BF7	3	0.18	0.056	0.47	0.41	0.15
Copolymer film BF6	3	0.079	0.026	0.56	0.53	0.20
Copolymer film BF5	3	0.040	0.013	0.69	0.65	0.31
Copolymer film BF4	3	0.013	0.0043	0.81	0.79	0.51
Copolymer film BF3	3	0.012	0.0040	0.96	1.11	0.75
Copolymer film BF2	3	0.010	0.0033	1.25	1.41	0.99
Copolymer film BF1	3	0.004	0.0013	1.46	1.62	1.37
Homopolymer film of OFCB	3	0	0	1.62	1.67	1.63

The benzene feed location was always in the DS.

Adding a very small amount of benzene to initiate copolymerization leads to a dramatic change in deposition rate as shown in Fig. 2 for all three feed locations. At a $b/(b+f)$ ratio of 0.004, the film deposition rates increased to 3.3, 5.5, and 8.7 nm/min for the DS, PE, and PZ, respectively. The addition of a small volume of benzene essentially doubles the film deposition rates. With continued addition of benzene, the deposition rates continue to increase and eventually reach a plateau. Both traits are attributed to the rapid step-growth mechanism (RSGP) [9].

According to the principles of RSGP, the growth of plasma polymers is dependent upon the formation and dissipation of the activated species from the monomers. Different from conventional 'wet' chain-growth polymerization, the sequence of formation and dissipation reactions in plasma polymerizations are not sequential but independent [9]. During the collision initiation of benzene and OFCB, two major synthetic routes are involved: Creation of monofunctional activated species, $M\cdot$, by dehydrogenation and defluorination and creation of difunctional and/or multifunctional intermediates, $\cdot M\cdot$ by opening of π-bond connections of benzene and the breaking of a cyclic structure (for both benzene and OFCB) as shown in reactions (1)–(4) [9,32]. The subscripts i, j, or k indicate the difference in size of the species involved with $i \leq j \leq k$ ($i = j = k$ is possible). Although the activated species are represented by the free radical symbol ($M\cdot$), any activated species including ions and excited molecules can be considered.

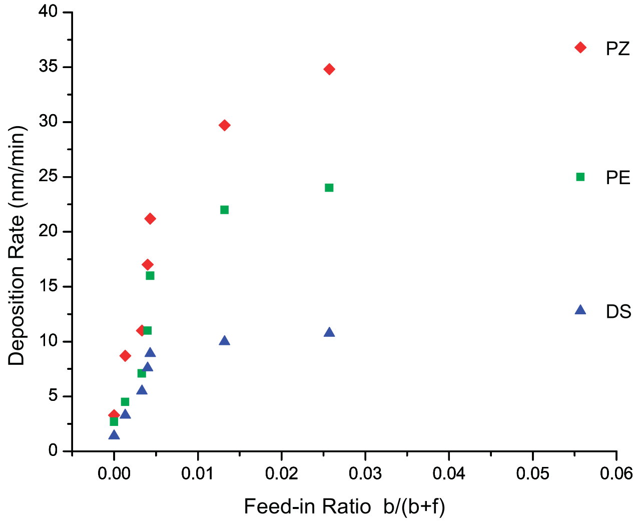

Fig. 2. Film deposition rate vs. the comonomer feed ratio, $b/(b+f)$, at the three different OFCB feed locations, PZ, PE and DS.

Propagation

$$M_i\cdot + M \rightarrow M_i - M\cdot \tag{1}$$

$$\cdot M_k\cdot + M \rightarrow \cdot M_k - M\cdot \tag{2}$$

$$\cdot M_j\cdot + \cdot M_k\cdot \rightarrow \cdot M_j - M_k\cdot \tag{3}$$

$$M_i\cdot + \cdot M_k\cdot \rightarrow M_i - M_k\cdot \tag{4}$$

Termination

$$M_i\cdot + \cdot M_j \rightarrow M_i - M_j \tag{5}$$

$$\cdot M_j\cdot + \cdot M_k\text{-}M_i\cdot \rightarrow \begin{array}{c} M_j \\ / \quad \backslash \\ M_i — M_k \end{array} \tag{6}$$

For benzene monomers, initiation forms predominantly difunctional and multifunctional species due to the conjugated ring structure, whereas for OFCB, collision with the energized species forms either difunctional intermediates due to the ring opening or monofunctional species due to the dissociation of fluorine. Termination occurs as described in reactions (5) and (6) [9,32], although the formation of many activated aliphatic and vinyl species by breaking benzene monomer rings allows the possibility of disproportionation. For homopolymerization, the OFCB deposition rate was much lower than that of benzene under similar reaction conditions. This is attributed to the much higher rate of self-termination of the fluorine-rich excited species leading to the formation of non-reactive low

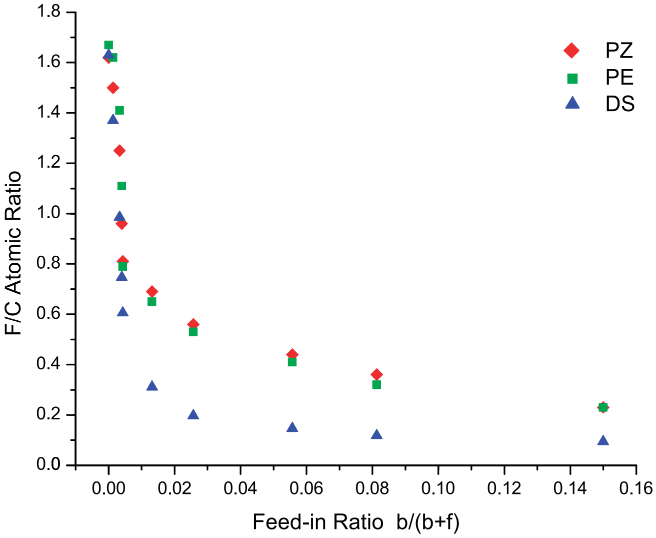

Fig. 3. Variation of the F/C ratio (determined by XPS measurements) in the films as a function of the monomer feed ratio, $b/(b+f)$, at the three different OFCB feed locations, PZ, PE and DS.

molecular weight materials, which are removed by the vacuum pumps. However, during plasma copolymerization, some of the activated fluorine species collide with the activated bifunctional/multifunctional hydrocarbon species initiated from the benzene monomers. These combinations create activated fluorine-containing species which participate in the copolymerization, leading to a significant decrease in self-termination of fluorine species.

A notable feature of the plasma homo-/copolymerization chemistry when employing OFCB is defluorination [28]. As shown in Table 1 and Fig. 3, the F/C stoichiometry of plasma polymerized OFCB films is fluorine deficient as compared to the starting OFCB monomer or conventional poly(tetrafluoroethylene) (PTFE). For OFCB homopolymerization, no significant film composition difference with respect to feed locations was observed, as film F/C ratios of 1.62, 1.65, and 1.63 for the PZ, PE, and DS feed locations, respectively, were determined by XPS (seen in Table 1, and Fig. 3). This is confirmed in Fig. 4 as the FT-IR spectra show nearly identical features including a strong broad band near 1100–1400/cm due to the convolution of stretching modes of a variety of fluorocarbon moieties, small peaks at 740 and 1740/cm due to absorption from amorphous fluorine structural units, and small peaks in the 2800–3000/cm region which represent aliphatic moieties formed during the plasma polymerization [26]. Thus, both IR and XPS data indicate that the chemical composition and structure of these homopolymerized OFCB films are quite similar to each other, although their film growth rates are rather different.

Upon addition of a small amount of benzene, a significant decrease in the fluorine content for the copolymerized films was observed (much more than due to dilution itself). These defluorination trends relative to input concentration resemble each other for all feed locations (as seen in Fig. 3 and Table 1). This defluorination can be attributed to fluorine loss caused by debonding of fluorine from C–F units in addition to the elimination of excited fluorine species by collision with benzene molecules. The decrease in the F/C ratio of the DS films was much faster than those for the PZ and the PE films. A $b/(b+f)$ feed ratio of 0.013 leads to a F/C value of 0.51 for the DS films, which is only 63% of the corresponding F/C value of PE or PZ films. The low bond dissociation energy (2.74 eV for opening a π-bond) of benzene leads to a higher probability of activation and fewer activated fluorine species. This is in contrast to the behavior in the PE or PZ locations, where OFCB is initiated exclusively without any competition from benzene molecules.

Fig. 5 shows the FT-IR spectra of PECVD copolymerized films with the same comonomer feed ratio (0.0043) at

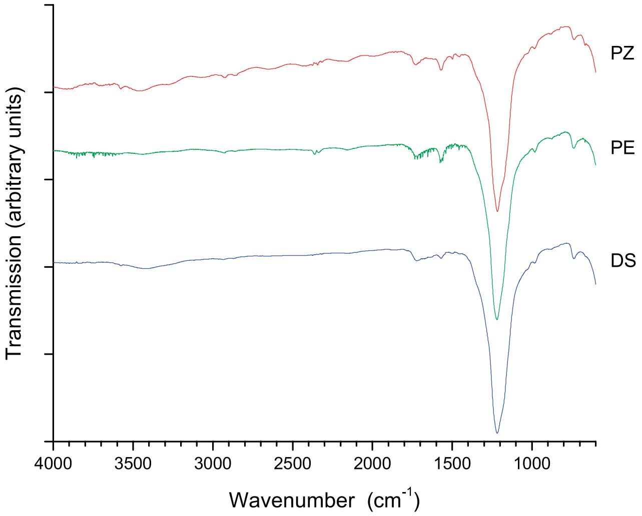

Fig. 4. FT-IR spectra for the plasma homopolymerized OFCB films at the three different OFCB feed locations, PZ, PE, and DS.

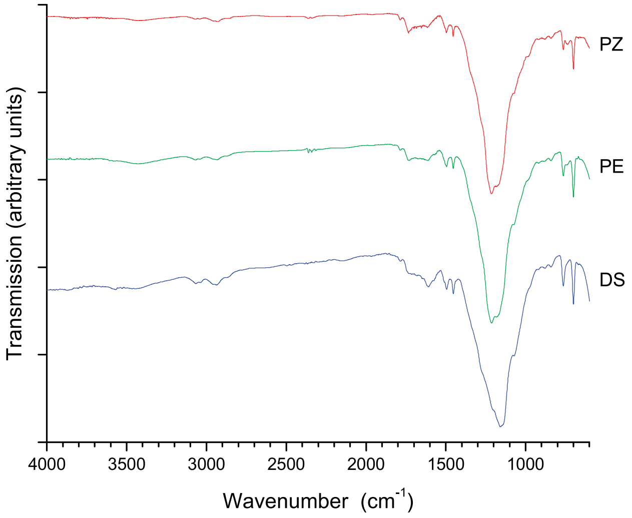

Fig. 5. FT-IR spectra of the PECVD copolymerized films with the same comonomer feed ratio (0.0043) but with the OFCB fed into the chamber at the three different locations, PZ, PE and DS.

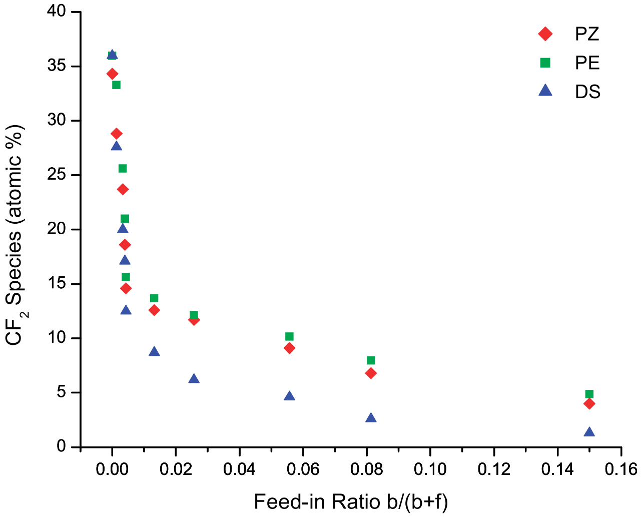

Fig. 6. Variation of the CF_2 at.% in the resultant films with the comonomer feed ratio, $b/(b+f)$, at the three different OFCB feed locations, PZ, PE, and DS.

three different feed locations. Compared with the IR spectra of OFCB homopolymerized films (Fig. 4), the copolymerized films maintain a strong CF_x vibration band at 1100–1400/cm, although this band is broader and weaker especially for the DS film. These spectra also indicate that other structural moieties from the hydrocarbon species are formed in the DS location, whose vibrations mix with those of CF_x moieties. The peaks at 699 and 762/cm, denoting the aromatic ring vibrations, become quite distinct for the DS films. Peaks in the 3000–3100/cm region, corresponding to aromatic C–H stretching emerge. A vibration at 1506/cm corresponding to C=C ring stretching in $–C_6H_5$, and a few weak bands near 700–900/cm, all seen clearly in the DS films, indicate that aromatic conjugation structures are present. This is true for the PE and the PZ films as well, and the IR spectra of the PE and PZ films appear similar. As the $b/(b+f)$ ratio increases, the decrease in F/C ratio of the PECVD copolymerized films reaches a plateau. This phenomenon is primarily due to the precursor feed method. As listed in Table 1, the OFCB feed rate was initially maintained constant (3 cm^3/min) while the benzene feed rate was increased. After reaching the maximum benzene content (0.18 cm^3/min), the OFCB feed rate was subsequently decreased. The activated hydrocarbon species gradually become the dominant source for the increase of non-fluorine structural units in the films.

As discussed previously [28], the different fluorine-containing structural moieties showed contrasting behaviors. By curve fitting the C 1s XPS data, the changes of individual $CF_{x(x=1-3)}$ components in the films for the different feed locations were obtained. Fig. 6 shows the variation of CF_2 at.% in the resultant films as a function of the comonomer feed ratio, $b/(b+f)$, for the three feed locations. For OFCB plasma homopolymerized films, the CF_2 content is nearly the same regardless of the feed location, 36.0, 36.0, and 34.4% for the DS, PE, and PZ location, respectively. As benzene was added, the CF_2% dropped significantly for all three OFCB feed locations, similar to the sharp drop in the overall F/C ratio of the films shown in Fig. 3. The variation of CF_3 groups with increasing benzene share a similar resemblance to the CF_2 moieties for all three feed locations, with a monotonic decrease, as shown in Fig. 7.

The CF concentration increased with the addition of benzene for all three OFCB feed locations and then decreased with increasing benzene concentration as shown in Fig. 8. The homopolymerized films had approximately the same concentration, 23.4, 23.4, and 22.9% for PZ, PE and DS, respectively. Although the general trends for the CF concentration for all three feed locations were similar, some

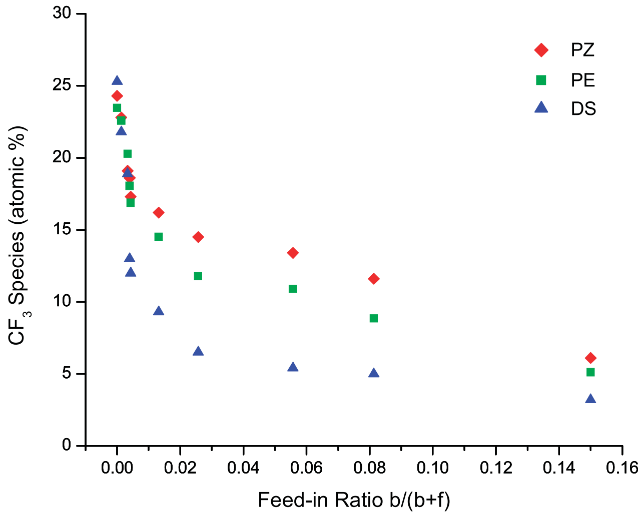

Fig. 7. Variation of the CF_3 at.% in the resultant films with the comonomer feed ratio, $b/(b+f)$, at the three different OFCB feed locations, PZ, PE, and DS.

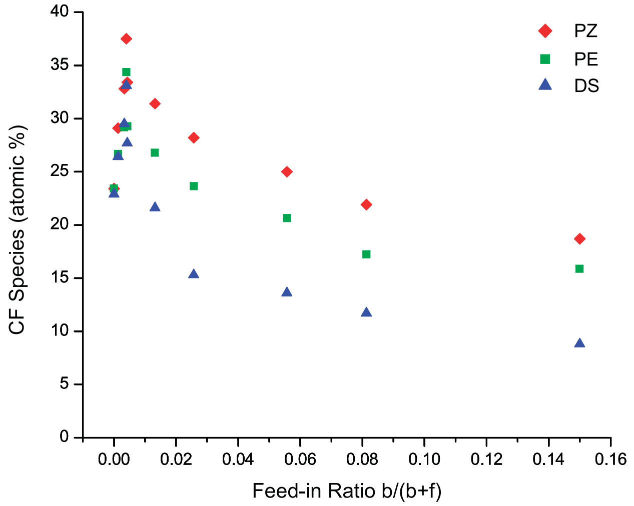

Fig. 8. Variation of CF at.% in the resultant films with the comonomer feed ratio, $b/(b+f)$, at the three different OFCB feed locations, PZ, PE, and DS.

specific differences exist. For the PZ film, the CF content had the biggest increase compared to the other two films, the maximum value reaching 38% and dropping to 19% at a $b/(b+f)$ ratio of 0.15, the CF content was still 19%. On the contrary, the DS films had the lowest CF content at all the corresponding points, its maximum being about 33%, dropping to only 9%. Values for the PE films were intermediary with a maximum of 34% and a low value of 16%.

In general, for all copolymerized films, the F/C ratio declined with the addition of benzene. The DS films had the most significant decrease in CF_2 and CF_3 percentages, as described above. The total $CF_{x(x=1-3)}$ content decreased from 84% for the homopolymerized film to 40% at a $b/(b+f)$ of 0.013. Correspondingly, the decrease for the PZ and the PE films were relatively mild as the content was still greater than 50% at a $b/(b+f)$ of 0.013 for both films (60% for PZ and 55% for PE). All these phenomena confirm that the film deposition mechanisms in the downstream region for the OFCB homopolymerized films are similar regardless of the monomer feed location. This is not the case, however, for copolymerization as the monomer feed location leads to significant differences in the composition and structure of the copolymerized films.

Activated fluorine species are created by the decomposition of OFCB through collision-induced reactions including electron impact dissociation, ion bombardment, and collision with argon metastable species, in addition to radiation-induced reactions including unimolecular excitation and dissociation [13,33,34]. As discussed above, the high reactivity of benzene molecules seriously affects the initiation of the fluorine species when introduced in the DS region, leading to a significant decrease in the quantity of activated fluorine species available for copolymerization. For the PE and PZ locations, OFCB is initiated exclusively leading to the formation of a large concentration of activated fluorine species. There is, however, a certain probability that a portion of the activated CF_2 species undergoes recombination to form other reactive species, in the reaction area. These species include the formation of activated CF species by depletion of fluorine from CF_2, the creation of activated CF_3 by the unimolecular rearrangement and bimolecular disproportions: $CF_x+CF_x \rightarrow CF_{x-1}+CF_{x+1}$ [28,35]. It is interesting to note that the concentration patterns of the CF_x moieties in the resultant films are consistent with the changes in these reactions caused by the different feed locations. Variations in the chemical composition and structure of the copolymerized films are created by the combination of the formation of different quantities of activated fluorine species through the change of the OFCB feed location, and the selectivity of benzene molecules' ability to react with various fluorine species. Clearly, more research is needed to further clarify this behavior.

Fig. 9 shows the refractive index (RI) vs. the F/C ratio of the PECVD films for the three OFCB feed locations. Assuming the regression of all the data points has a formula of $n=a+bX$, we obtain a straight line with $a=1.6797$ and $b=-0.1827$, as well as $R=-0.993$. Regression analysis for any of the individual feed locations yields similar results indicating that the refractive index of the plasma polymerized films is basically a function of the F/C ratio. Thus, as expected, the film refractive index is determined primarily by the film's chemical composition. This behavior also implies that the film deposition mechanism at the substrate for all three different OFCB feed locations is similar. It is well known that the proportion of conjugated hydrocarbon units in the PECVD film affects the refractive index of the film [28]. Larger amounts of conjugation present in the film would yield higher refractive indices. Since we obtain nearly similar RIs for the films with the same F/C ratio but different OFCB feed locations, the same conjugated hydrocarbon structural moieties are present in the final film composition.

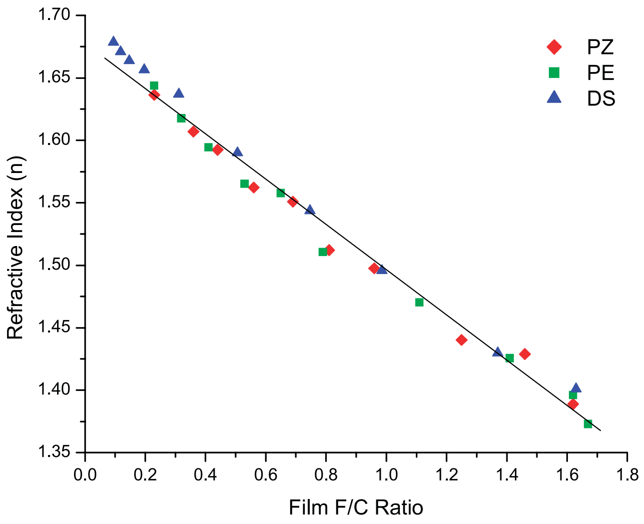

Fig. 9. Refractive index of the resultant PECVD films vs. film F/C ratio at the three OFCB feed locations, (◆) PZ, (■) PE and (▲) DS.

4. Conclusions

Three monomer feed locations, DS, PE, and PZ, for OFCB plasma homopolymerization, lead to substantially different deposition rates but similar chemical composition of the polymerized films. This implies that under our experimental conditions, film deposition on the substrate follows similar mechanisms. The deposition rate is highest for initiation in the highly energetic plasma zone as expected. Addition of a small amount of benzene at a fixed downstream location leads to much higher film deposition rates. This behavior illustrates the complexity of plasma copolymerization. Due to the low dissociation energy for breaking π-bonding, the benzene monomers have a much higher initiation probability as compared to OFCB molecules. These mechanisms of collision-mediated-energy-transfer and rapid step-growth plasma polymerization lead to a decrease of activated fluorine species available for copolymerization. Addition of a small amount of benzene gives rise to substantial defluorination of the polymerized films whose magnitude is significantly influenced by the input location of the OFCB monomer. All these results indicate that a small amount of benzene comonomer affects the gas-phase initiation, propagation, and termination reactions, resulting in differences in the chemical composition and structure of the PECVD films at different OFCB feed locations. However, the final refractive index of the resultant PECVD films was observed to primarily depend on the film F/C ratio.

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