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Diverse Amorphous Carbonaceous Thin Films Obtained by Plasma Enhanced Chemical Vapor Deposition and Plasma Immersion Ion Implantation and Deposition

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Abstract

Diverse amorphous hydrogenated carbon and similar films containing additional elements were produced by Plasma Enhanced Chemical Vapor Deposition (PECVD) and by Plasma Immersion Ion Implantation and Deposition (PIIID). Thus a-C:H, a-C:H:F, a-C:H:N, a-C:H:Cl and a-C:H:O:Si were obtained, starting from the same feed gases, using both techniques. The same deposition system supplied with radiofrequency (RF) power was used to produce all the films. A cylindrical stainless steel chamber equipped with circular electrodes mounted horizontally was employed. RF power was fed to the upper electrode; substrates were placed on the lower electrode. For PIIID negative high tension pulses were also applied to the lower electrode. Raman spectroscopy confirmed that all the films are amorphous. Chemical characterization of each pair of films was undertaken using Infrared Reflection Absorption Spectroscopy and X-ray Photoelectron Spectroscopy. The former revealed the presence of specific structures, such as C-H, C-O, O-H. The latter allowed calculation of the ratio of hetero-atoms to carbon atoms in the films, e.g. F:C, N:C, and Si:C. Only relatively small differences in elemental composition were detected between films produced by the two methods. The deposition rate in PIIID is generally reduced in relation to that of PECVD; for a–C:H:Cl films the reduction factor is almost four.

Keyword：carbonacous thin films, XPS, IRRAS, Raman spectroscopy

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Keywords: PECVD, PIIID, XPS, IRRAS

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1. Introduction

Amorphous hydrogenated carbon, a-C:H, films may be produced by Plasma enhanced chemical vapor deposition (PECVD) [1, 2]. Similar films such as a-C:H:F [3, 4], a-C:H:N [5, 6] and a-C:H:O:Si [7, 8] have also been created using this technique. Polypropylene surfaces have been chlorinated using plasmas of CCl_4 [9] and $CHCl_3$ [10]. Doping of pyrrole and thiopene plasma polymers with chlorine via copolymerization with chloroform has also been reported [11]. Plasmas fed monomers such as acetylene [3] or benzene [4] serve to form a-C:H films; plasmas fed benzene/octafluorocyclobenzene mixtures [12] can form a-C:H:F, while plasmas of hexamethyldisiloxane/oxygen mixtures [13] produce a-C:H:O:Si. Films of the type a-C:H, a-C:H:F, a-C:H:N and a-C:H:Si:O find application, amongst others, in optical storage [2] and resistive switching memory [14], layers transparent in the infrared region [3], heterojunction diodes [15], and haemocompatible coatings [16], respectively.

Plasma excitation in PECVD is traditionally via a radiofrequency field applied to the cathode. In ion implantation by immersion in plasma (IIIP), high voltage negative pulses are applied to the anode. This may be done in an inert gas or in a polymerizing atmosphere. In the latter both deposition and ion irradiation occur.

Ion implantation in conventional polymers is known to influence the film structure, typically releasing hydrogen and other volatile species and producing film compaction [17]. Energetic ions collide with the atoms of the polymer, breaking chemical bonds, causing ionization, and the excitation of phonons [18]. The presence of ions, excited molecules and their fragments induce chemical changes via free radical reactions.

PIIID of a-C:H films from C_2H_2-Ar mixtures produces films with a surface hardness of ~ 6 GPa, which is about an order of magnitude greater than is typical of similar films produced without ion implantation [19]. By applying high-voltage negative pulses to the substrate holder in the presence of hydrocarbon or other carbon-based molecules, ions such as CH_x^+ are accelerated towards the substrate where they impact with high kinetic energy, and may be implanted into the film. Diamond-like carbon films with hardnesses in the range of 5 to 25 GPa have also been produced from C_2H_2, depending on the pressure (1 to 15 mtorr) and the pulse voltage (-0.2 to -4.0 kV) [20]. Recent developments in the PIIID of diamond-like carbon (DLC) films have been authoritatively reviewed by Ensinger [21].

Yang et al. [22] produced a-C:H:N films by the PIIID of C_2H_2-N_2 mixtures. Films containing more nitrogen showed increased surface roughness and lower water contact angles. Such films may be useful for applications requiring good blood compatibility. By CF_4 PIIID of a DLC layer, Yao et al. [23] fabricated a-C:F films. At high CF_4 flow rates, F_R, (~ 8 sccm), surface contact angles close to that of Polytetrafluoroethylene (PTFE) (108°) were produced. Although the nano-hardness of the films reduced with increasing F_R, they were still an order of magnitude greater than PTFE (0.8 GPa). Oxygen plasma treatment of plasma polymerized HMDSO increases both the surface hardness of the films and their wettability [24].

In this study a-C:H, a-C:H:F, a-C:H:N, a-C:H:Cl and a-C:H:Si:O were produced by PECVD and by PIIID. The deposition conditions were maintained constant except for the application of a pulsed negative high tension to the substrate holder during PIIID. Differences in the chemical structure were sought via Raman spectroscopy, infrared reflection absorption spectroscopy (IRRAS) and X-ray photoelectron spectroscopy (XPS).

2. Experimental

Films were produced by PECVD and by PIIID in the system outlined in Figure 1 and described in the literature [25]. Briefly, this consists of a cylindrical stainless-steel chamber fed gases from cylinders via regulators and needle valves or monomer vapors via a vial of liquid monomer sealed by a needle valve. The chamber contains horizontal parallel-plate electrodes. Radiofrequency power (45 to 100 W) is fed to the upper electrode via a matching circuit. For PECVD the lower electrode (anode) is grounded. For PIIID the upper electrode (cathode) continues to be fed RF power, while the lower electrode receives negative 20 μs pulses of up to 4000 V produced using a RUP 6-20 supply (GBS Elektronic, GmBH, Germany). During deposition the system was evacuated continuously using a rotary vane pump. The partial pressures in the absence of the discharge were used as control parameters.

Five pairs of films were produced by PECVD and PIIID. For the deposition of each pair the chamber was fed the same monomer/comonomer under the same conditions of pressure and applied RF power. The five feeds (with the partial pressures in Pa), were, respectively, benzene (13.3)/argon (4.0), benzene (13.3)/sulfur hexafluoride (5.3), benzene(8.0)/nitrogen(5.3), acetylene(3.3)/chloroform(10.0), hexamethyldisiloxane (HMDSO)(13.3)/argon(6.7). The substrates were placed on the lower electrode for all the depositions. Deposition times of 15 to 25 min. were used. Films for perfilometry, IRRAS, and XPS were deposited on glass, aluminum-coated glass slides and aluminum plates, respectively. A mask, which partially covered a glass substrate, was used to produce a well-defined step-height from which the film thickness was obtained using a profile meter (Vesco, Dektak^{3}ST). Raman spectroscopic analysis in the 1200 to 2000 cm^{-1} range of each film (deposited onto a silicon substrate) was carried out using a Renishaw 2000 system with an Ar$^+$ laser (λ = 514 nm), in backscattering geometry, which produced a laser power of ~0.6 mW on the sample surface. The laser spot had a diameter of ~2.5 mm. The measurements were carried out in air at room temperature.

Infrared spectra were obtained in the 400 to 4000 cm^{-1} range at near normal incidence using a Jasco FT/IR-410 spectrophotometer (Jasco, Easton, MD, USA). In addition, spectra were obtained at grazing incidence using a Bowen MB-101 Fourier Transform Infrared spectrophotometer equipped with a variable angle attachment. X-ray photoelectron spectroscopy measurements were obtained using a VG Microtech ESCA 3000 (with MgK$_\alpha$ and AlK$_\alpha$ radiations) spectrometer. A take-off angle of 45° to the sample normal was employed in a hemispherical energy analyzer with an overall energy resolution of about 0.8 eV. Widescan and Gaussian deconvoluted C1s spectra were obtained. Shirley background correction was employed.

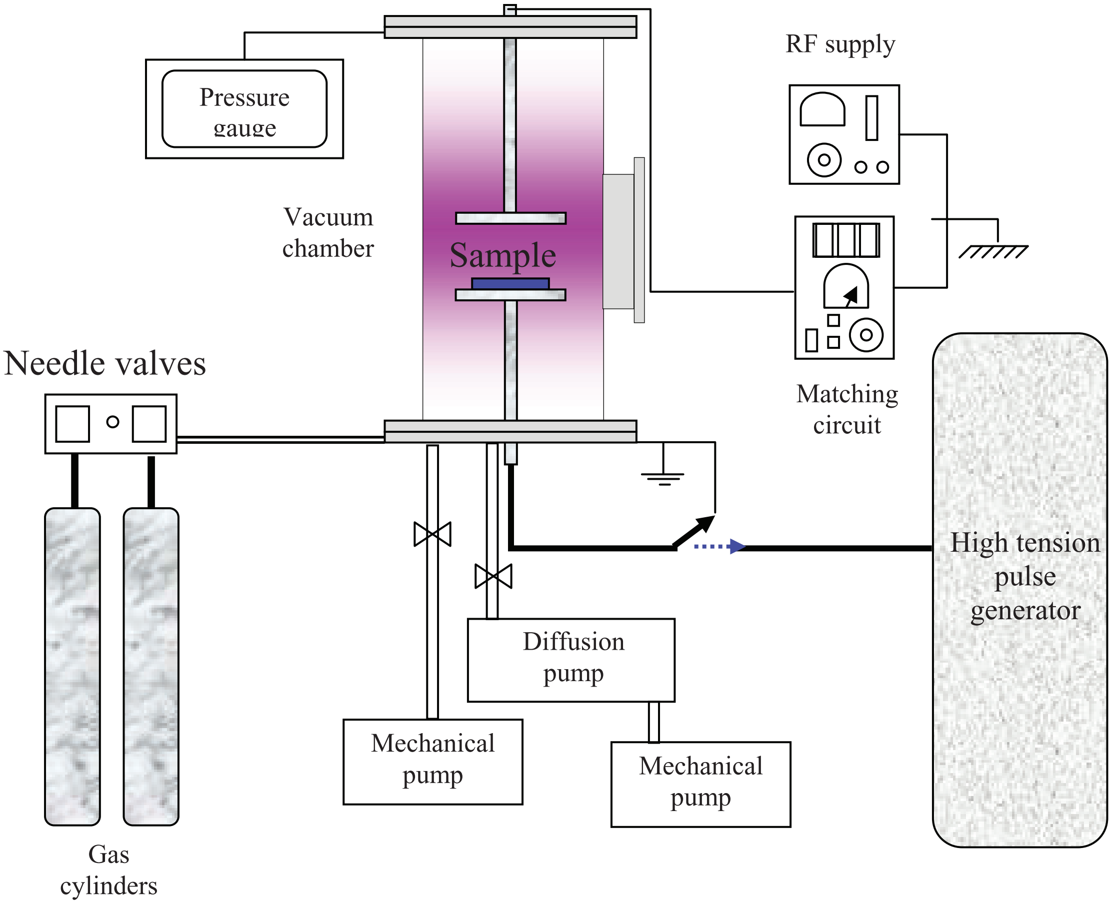

Figure 1. System for Plasma Enhanced Chemical Vapor Deposition (PECVD) and Plasma Immersion Ion Implantation and Deposition (PIIID).

3. Results and Discussion

3.1 Film Thickness

The film thicknesses for each pair of films are listed in Table 1. Under the same conditions the film thickness is typically reduced with PIIID compared to that obtained by PECVD. It is known that ion implantation of films fabricated by PECVD produces compaction and the loss of hydrogen. For example, PECVD films from plasmas of C_6F_6 subsequently subjected to helium plasma immersion implantation are reduced to ~60% of their original thickness [26]. The present results indicate that with PIIID film compaction occurs (relative to films grown by PECVD) over a range of films with somewhat different compositions. Compactions by a factor of roughly two were typical. An exception to this tendency is the pair of a-C:H:Si:O films, for which ion implantation increases the film thickness. This is unexpected but since neither of the deposition conditions was systematically optimized it may be that they were closer to optimal for the PIIID, leading to a higher deposition rate.

Table 1. Film thickness as measured using a profile meter.

Monomer/Comonomer	**Thickness (nm)**	
	PECVD	**PIIID**
C_6H_6 + Ar	**495 ± 23**	**293 ± 42**
C_6H_6 + SF_6	**3347 ± 475**	**1796 ± 39**
C_6H_6 + N_2	**548 ± 25**	**375 ± 31**
$CHCl_3$ + C_2H_2	**1166 ± 29**	**313 ± 12**
HMDSO + Ar	**518 ± 26**	**929 ± 113**

3.2 Raman Analysis

Raman spectra between 1200 and 2000 cm^{-1} of all the films (not shown) were featureless, revealing no peak at 1332 cm^{-1} (expected from diamond), or any band in the 1450 to 1650 cm^{-1} region (expected from graphite). Thus the films were amorphous.

3.3 Infrared Analysis

Figures 2(a, e) show the infrared spectra in the 400 to 4000 cm^{-1} range for the five pairs of films.

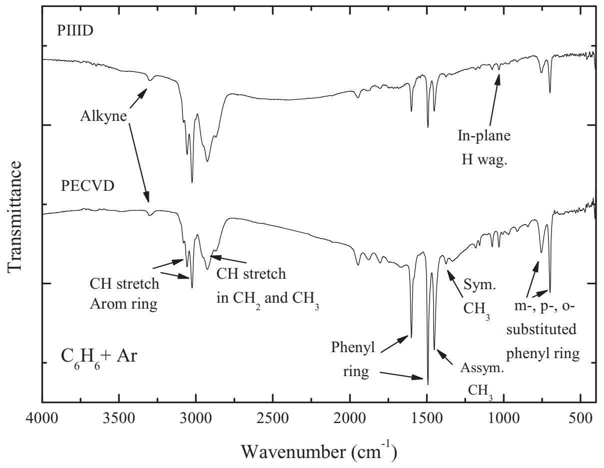

Fig. 2a. Transmission infrared spectra of the films produced from plasmas of benzene and argon by PECVD and PIIID.

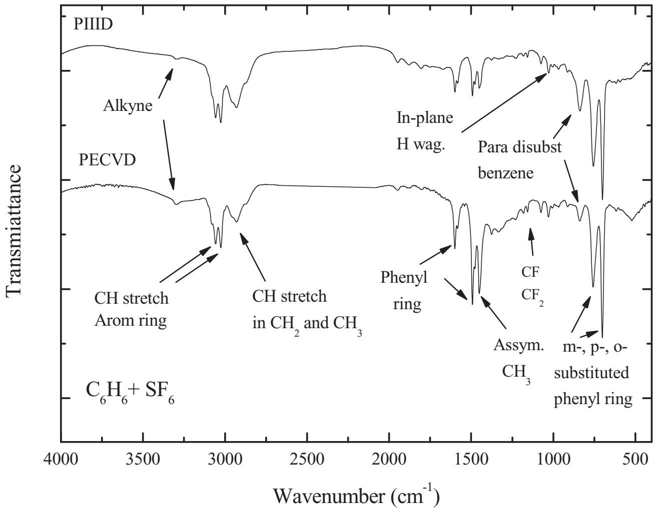

Figure 2b. Transmission infrared spectra of the films produced from plasmas of benzene and sulfur hexafluoride by PECVD and PIIID.

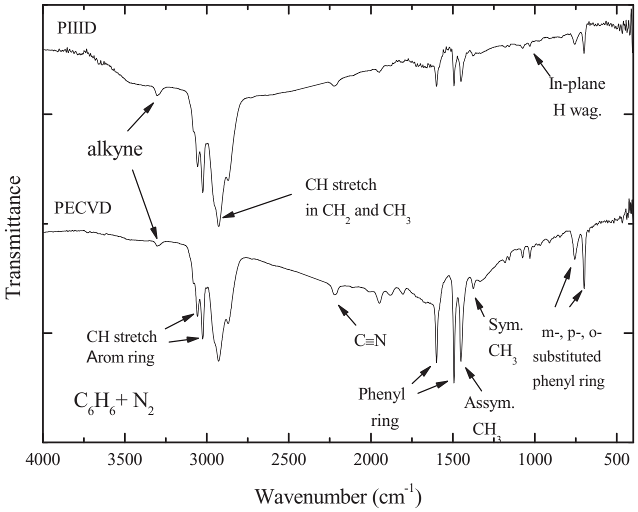

Figure 2c. Transmission infrared spectra of the films produced from plasmas of benzene and nitrogen by PECVD and PIIID.

The spectra of the films produced with benzene in the chamber feed (spectra of Fig. 2a, Fig. 2b and Fig. 2c) exhibit bands characteristic of aromatic rings, indicating the partial preservation of the monomer structure in the deposited material. For example, the bands due to CH stretching in the aromatic ring at 3030 and 3060 cm^{-1}, and those due to vibrations in the phenyl rings at 1500 and 1600 cm^{-1}. In addition, there are bands due to *meta-, para-* and *ortho-* substituted phenyl rings peaked at 700 and 760 cm^{-1}. Associations of these structures with these frequencies are found in the literature [4]. A prominent peak at around 1440 cm^{-1} is also observed in the spectra of Figs. 2a to 2c, together with a much less prominent band at about 1375 cm^{-1}. These are attributable to asymmetric and symmetric bending modes in CH_3 groups, respectively [3]. As none of the monomers contain methyl groups, these can only be produced via multiple-step reactions in the plasma or via plasma/film reactions or both. An intense band centered at about 2930 cm^{-1} is seen in all the spectra of Fig. 2a to Fig. 2c, and is due to CH stretching in CH_2 and CH_3 groups. Small absorption bands due to in-plane hydrogen wagging at a little more than 1000 cm^{-1} are also visible in spectra a to c. All the spectra of Figs. 2a to 2c also show a small but clearly discernible absorption band at 3300 cm^{-1}. This is attributed to the presence of alkynes, i.e. C≡C structures. Such triple bonds are not present in the monomer benzene, and must therefore have been produced in the discharges or on the growing film. This possibly occurs via the decyclization of the benzene ring.

Close inspection of the spectra of Fig. 2b reveals the emergence of small bands at about 1100 cm^{-1} and 1210 cm^{-1}, which is attributed due to CF stretching in CF and CF_2 groups, respectively [27]. Also seen in the spectra of Fig. 2b, is a band centered at about 830 cm^{-1}, which may be attributed to *para* disubstituted benzene. The spectra of Fig. 2c are of the films obtained with nitrogen in the chamber feed. A feature of these spectra is the emergence of a small but distinct band at about 2200 cm^{-1} due to the presence of nitrile groups.

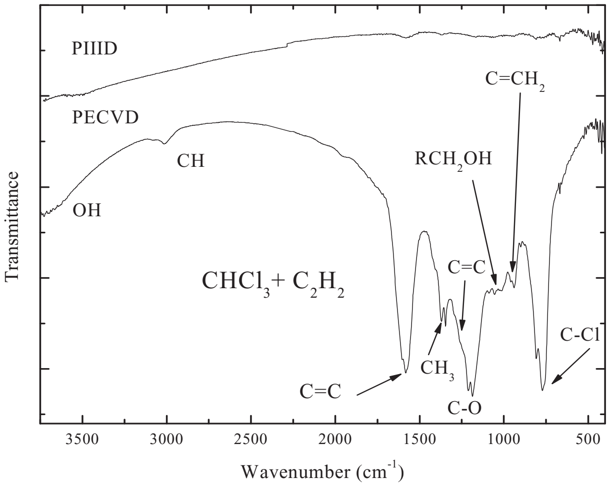

Figure 2d. Transmission infrared spectra of the films produced from plasmas of acetylene and chloroform by PECVD and PIIID.

Spectra of the films produced from plasmas of acetylene and chloroform are shown in Figure 2d. The principal peaks and their attributions are indicated. As the PIIID film is much thinner than that produced by PECVD, the absorptions are smaller. The films are chlorinated plasma polymers as revealed by the presence of CH_2, CH_3, C=C and C-Cl groups. The following attributions are made: OH (broad band ~3500 cm^{-1}); CH (~3000 cm^{-1}); C=C (~1570 cm^{-1}); CH_3 (~1360 cm^{-1}); C=C (~1260 cm^{-1}); C-O (~1180 cm^{-1}); RCH_2OH (~1050 cm^{-1}); $C=CH_2$ (~950 cm^{-1}); C-Cl (~770 cm^{-1}).

Several specific interactions may be deduced from the film structure. Neither CH_2 nor CH_3 groups are present in the monomers, therefore multiple reactions, perhaps via hydrogen addition by opening of the acetylene triple bond, must be responsible for their production. In addition, C=C bonds are not present in the monomers. If these bonds derive from C≡C, they probably occur by the addition of hydrogen. Some oxygen-containing species such as C-O and O-H are present despite the absence of oxygen in the plasma feed. For plasma polymers, however, it is well known that post-deposition reactions between free radicals trapped in the film and ambient air and water vapor lead to the presence of oxygen-containing functionalities on the film surface [28]. In the present study, although not always evident from the IRRAS spectra alone, the film surfaces always exhibit a minimum oxygen contamination (even when no oxygen is introduced into the gas feed), and this is confirmed by the XPS analyses reported in the following section.

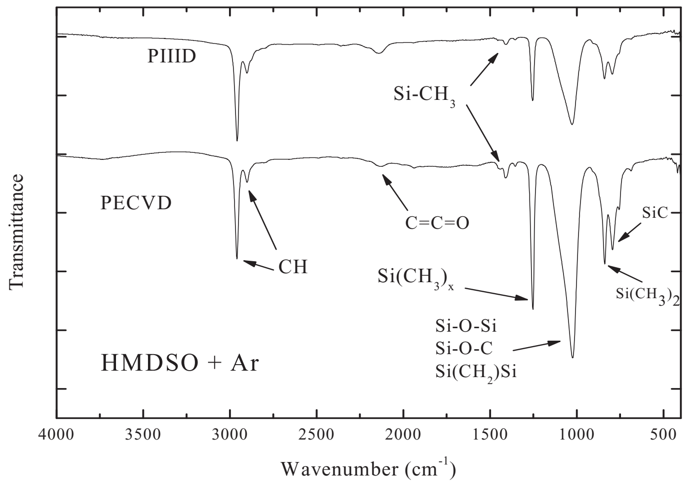

Figure 2e. Transmission infrared spectra of the films produced from plasmas of hexamethyldisiloxane and argon by PECVD and PIIID.

Figure 2e shows the spectra of the films obtained from plasmas of HMDSO and argon. There are many prominent bands in the spectrum of the film obtained by PECVD. The following may be identified: (a) CH bands peaked at (2960 and 2900 cm^{-1}); (b) C=C=O bands at ~ 2100 cm^{-1} (c) Si-CH_3 (~1410 cm^{-1}); (d) Si-$(CH_3)_x$ (~1250 cm^{-1}); (e) asymmetric stretching in Si-O-Si, Si-O-C and Si-(CH_2)-Si at ~1050 cm^{-1}; (f) rocking band due to $Si(CH_3)_2$ at ~830 cm^{-1}; (g) stretching in Si-C at ~800 cm^{-1}[29]. The structures CH, Si-$(CH_3)_x$, with x from 1 to 3, Si-O-Si and Si-C can all be produced from the monomer molecule by severe or mild fragmentation, depending on the case. The formation of Si-O-C structures, however, requires multiple reactions. Multiple bonds are also present in the films but absent from the monomer.

There are apparently no striking differences between the members of the pairs of spectra that may be attributed to the different deposition technique. All the films were also examined using IRRAS at grazing angle incidence, which can sometimes reveal additional bands not observed with normal incidence. These spectra (not shown) were consistent with the near-normal IRRAS spectra. The fluorine-related bands seen in the spectra of the a-C:H:F films were stronger.

3.4 X-ray Photoelectron Spectroscopy

Widescan spectra of each film in the 0 to 1100 eV range allow identification of the principal elements present. Elemental concentrations calculated using such spectra are illustrated in Table 2.

In Table 2 the hydrogen content of the films, which is not accessible to XPS, has been ignored. The films deposited from benzene (and argon) are hydrogenated carbon films, which also contain some oxygen. As mentioned above, post-deposition oxygenation is known to occur in plasma polymers upon exposure to the laboratory environment [28]. Little systematic variation in the film elemental composition is produced by PIIID compared to PECVD.

Fluorine is incorporated into those films deposited with SF_6 in the feed. Fluorine contents of 4.5% and 3.1%, respectively, for films grown by PECVD and by PIIID are observed. Again, some oxygen is present despite its absence from the chamber feed. Some sulfur incorporation, of up to 2.5% is also observed for the films produced with SF_6 in the plasma feed. This is consistent with previous studies of films produced from plasmas of C_2H_2-SF_6 [3]

and C_6H_6-SF_6 [4] mixtures where some sulfur incorporation is expected. For example, XPS analyses of films produced from C_6H_6-SF_6 mixtures with 30% SF_6 in the chamber feed lead to an S:C ratio of 0.336 [4].

Table 2. Elemental composition determined by XPS of the films produced by PECVD and PIIID from the monomer/comonomer indicated

Monomer/Comonomer Method	**Elemental Composition (%)**						
	C	**O**	**N**	**F**	**S**	**Si**	**Cl**
C_6H_6 + Ar PECVD	**95.6**	**4.4**	**-**	**-**	**-**	**-**	**-**
C_6H_6 + Ar PIIID	**95.2**	**4.8**	**-**	**-**	**-**	**-**	**-**
C_6H_6 + SF_6 PECVD	**89.8**	**3.3**	**-**	**4.5**	**2.5**	**-**	**-**
C_6H_6 + SF_6 PIIID	**92.3**	**3.2**	**-**	**3.1**	**1.4**	**-**	**-**
C_6H_6 + N_2 PECVD	**93.1**	**5.8**	**1.1**	**-**	**-**	**-**	**-**
C_6H_6 + N_2 PIIID	**95.2**	**3.8**	**1.0**	**-**	**-**	**-**	**-**
$CHCl_3$ + C_2H_2 PECVD	**36.0**	**0.6**	**-**	**-**	**-**	**-**	**63.4**
$CHCl_3$ + C_2H_2 PIIID	**37.3**	**0.3**	**-**	**-**	**-**	**-**	**62.4**
HMDSO + Ar PECVD	**48.8**	**21.8**	**-**	**-**	**-**	**29.4**	**-**
HMDSO + Ar PIIID	**49.4**	**20.0**	**-**	**-**	**-**	**30.5**	**-**

The films deposited with nitrogen in the feed show low nitrogen contents (~1%). Films deposited from HMDSO and argon contain high carbon contents (approaching 50%), and high proportions of Si (~30%) and O (~20%). The ratio of the atomic number density of Si to O ~1.5, which is somewhat greater than the ratio of 0.5 expected of SiO_2..

The small fluorine and nitrogen components of the films deposited from benzene with SF_6 or N_2 in the chamber feed, respectively, are consistent with the infrared spectra of these films. There are no simple trends in the values of the compositions of the films obtained with PIIID compared to those obtained by PECVD.

Chlorine to carbon atomic number density ratios of ~1.8 were obtained for both the PECVD and PIIID films, indicating a high degree of chlorination. Oxygen incorporation was small (≤ 0.6 %).

Deconvolution of the C1s peaks of the a-C:H:F film spectra revealed contributions at 285 eV and 287.2 eV owing to C-H and possibly to β-shifted carbon (but contributions from CO and CS also fall at about this energy). The same deconvolution of the spectra of the a-C:H:Si:O films revealed contributions at about 285 and 287 eV for the PIIID films. The latter may be attributed to -CO groups [30]. Any contribution from C-Si (not observed) would be expected to fall at about 283.3 eV [31].

For the chlorinated films, deconvolution of the C1s peak revealed contributions at 285 eV due to CH and at ~286.4 eV, attributable to C-Cl. To account for the total Cl content of the films, part of it must be unbound.

4. Conclusions

Diverse amorphous hydrogenated carbon films (a-C:H, a-C:H:F, a-C:H:N, a-C:H:Cl and a-C:H:Si:O) were obtained by PECVD and PIIID. Under otherwise equal conditions, PIIID produced thinner films. As revealed by IRRAS and XPS the film structures produced by the two techniques are not markedly different.

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