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**THE RELATIONSHIP BETWEEN CHEMICAL  
STRUCTURE AND DIELECTRIC PROPERTIES OF  
PLASMA-ENHANCED CHEMICAL VAPOR DEPOSITED  
POLYMER THIN FILMS (POSTPRINT)**

**Kurt Eyink, Jesse Enlow, and Timothy J. Bunning**

**Hardened Materials Branch**

**Survivability and Sensor Materials Division**

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14. ABSTRACT Polymer dielectric films fabricated by plasma enhanced chemical vapor deposition (PECVD) have unique properties due to their dense crosslinked bulk structure. These spatially uniform films exhibit good adhesion to a variety of substrates, excellent chemical inertness, high thermal resistance, and are formed from an inexpensive, solvent-free, room temperature process. In this work, we studied the dielectric properties of plasma polymerized (PP) carbon-based polymer thin films prepared from two precursors, benzene and octafluorocyclobutane. Two different monomer feed locations, directly in the plasma zone or in the downstream region (DS) and two different pressures, 80 Pa (high pressure) or 6.7 Pa (low pressure), were used. The chemical structure of the PECVD films was examined by X-ray photoelectron spectroscopy and Fourier-transform infrared spectroscopy. The dielectric constant ( $\epsilon_r$ ) and dielectric loss ( $\tan \delta$ ) of the films were investigated over a range of frequencies up to 1 MHz and the dielectric strength (breakdown voltage) ( $F_b$ ) was characterized by the current-voltage method. <i>Abstract is continued on the reverse side</i>					
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#### 14. ABSTRACT (concluded)

Spectroscopic ellipsometry was performed to determine the film thickness and refractive index. Good dielectric properties were exhibited, as PP-benzene films formed in the high pressure, DS region showed a  $F_b$  of 610 V/ $\mu\text{m}$ , an  $\epsilon_r$  of 3.07, and a  $\tan \delta$  of  $7.0 \times 10^{-3}$  at 1 kHz. The PECVD processing pressure has a significant effect on final film structure and the film's physical density has a strong impact on dielectric breakdown strength. Also noted was that the residual oxygen content in the PP-benzene films significantly affected the frequency dependences of the dielectric constant and loss.

# The relationship between chemical structure and dielectric properties of plasma-enhanced chemical vapor deposited polymer thin films

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## Abstract

Polymer dielectric films fabricated by plasma enhanced chemical vapor deposition (PECVD) have unique properties due to their dense crosslinked bulk structure. These spatially uniform films exhibit good adhesion to a variety of substrates, excellent chemical inertness, high thermal resistance, and are formed from an inexpensive, solvent-free, room temperature process. In this work, we studied the dielectric properties of plasma polymerized (PP) carbon-based polymer thin films prepared from two precursors, benzene and octafluorocyclobutane. Two different monomer feed locations, directly in the plasma zone or in the downstream region (DS) and two different pressures, 80 Pa (high pressure) or 6.7 Pa (low pressure), were used. The chemical structure of the PECVD films was examined by X-ray photoelectron spectroscopy and Fourier-transform infrared spectroscopy. The dielectric constant ( $\epsilon_r$ ) and dielectric loss ( $\tan \delta$ ) of the films were investigated over a range of frequencies up to 1 MHz and the dielectric strength (breakdown voltage) ( $F_b$ ) was characterized by the current-voltage method. Spectroscopic ellipsometry was performed to determine the film thickness and refractive index. Good dielectric properties were exhibited, as PP-benzene films formed in the high pressure, DS region showed a  $F_b$  of 610 V/ $\mu\text{m}$ , an  $\epsilon_r$  of 3.07, and a  $\tan \delta$  of  $7.0 \times 10^{-3}$  at 1 kHz. The PECVD processing pressure has a significant effect on final film structure and the film's physical density has a strong impact on dielectric breakdown strength. Also noted was that the residual oxygen content in the PP-benzene films significantly affected the frequency dependences of the dielectric constant and loss.

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**Keywords:** Plasma enhanced chemical vapor deposition (PECVD); Polymer thin films; Dielectric properties; Structure

## 1. Introduction

Recently, considerable work has been undertaken to fabricate polymeric dielectric and photonic thin films using plasma enhanced chemical vapor deposition techniques (PECVD) [1–8] due to its room temperature, solvent-free and versatile operation. Many organic precursors can be selected to prepare thin polymer films with a wide range of compositions and chemical functionalities. Plasma polymerized (PP-) films, exhibiting highly crosslinked structures have been targeted for optical and dielectric applications such as waveguides, anti-reflection coatings,

band-gap filters for integrated optics, high performance capacitors and dielectric devices [9–13]. The focus of the current paper is the generation and evaluation of organic PECVD dielectric films with high dielectric strengths, moderately high dielectric constants and relatively low dielectric loss factors. An improved understanding of the composition/structure-property relationships is required to optimize the design and film fabrication for these various applications.

In this work, benzene and octafluorocyclobutane (OFCB) were chosen as starting precursors for exploring the relationship between structure and thin film dielectric properties. In order to study the effects of plasma-induced energetic species on the initiation and propagation of the plasma polymerization and film deposition, two monomer-feed locations and two reaction

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chamber pressure regimes were investigated. The PECVD films were characterized by Fourier-transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). Their dielectric properties were evaluated by established techniques, including measurements of dielectric constant ( $\epsilon_r$ ), loss factor ( $\tan \delta$ ), and breakdown strength ( $F_b$ ). The film thicknesses and optical refractive indices were determined by spectroscopic ellipsometry. Correlation of the composition and chemical structure with the dielectric properties of these PECVD films is discussed in detail.

## 2. Experimental details

Fig. 1 is a schematic of the PECVD set-up [14,15]. Briefly, 99.999% argon was used as the noble gas to flow into a 10 cm diameter glass reactor through a capacitively coupled, 13.56 MHz discharge. The diameter of the two coupling electrodes was 50 mm and the distance between them was 25 mm. The power for plasma generation could be controlled in the range of 20 to 75 W.

Two precursors were chosen for the fabrication of plasma homopolymerized thin films: benzene ( $C_6H_6$ , Aldrich Co., liquid, high performance liquid chromatography (HPLC) grade with a purity of 99.9%) and octafluorocyclobutane ( $C_4F_8$ , OFCB, SynQuest Laboratories, Inc., compressed gas, with a purity of >99%). Both of the monomers were used as received. For OFCB, the flow rate was controlled in the range of 0.5–3  $cm^3/min$ , and for benzene the vapor flow rates were in the range of 0.05–0.3  $cm^3/min$  (without any carrier gases). In order to keep a constant partial vapor pressure, a water-bath thermostat was used to maintain the temperature of the benzene reservoir at  $19.0 \pm 0.1$  °C.

Two reaction chamber pressures were applied during the study: 6.7 Pa labeled as the low pressure regime (L-) and 80 Pa labeled as the high pressure regime (H-). The chamber pressure described here was due both to the noble gas (argon) and monomer (OFCB or benzene vapor). A two-stage pumping system was used. In the first stage, a diaphragm vacuum pump (Model MD4C, Vacumbrand) was used instead of a rotary oil pump, in order to avoid oil contamination from back-streaming. In the second stage, a turbo-molecular pump (Model Turbo-V301 Navigator Pump, Varian) was used to keep the chamber vacuum close to  $10^{-4}$  Pa.

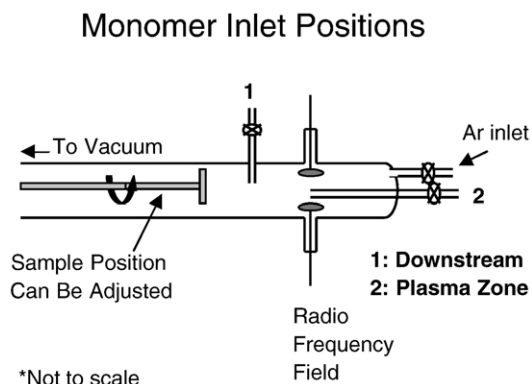


Fig. 1. Schematic of the PECVD set-up showing the two monomer inlet positions.

Processing conditions for this work included a plasma power of 45 W, argon flow rates of 20  $cm^3/min$  (for the low pressure regime) or 100  $cm^3/min$  (for the high pressure regime), with monomer feed locations either in the center of the plasma zone (PZ) or in the downstream region (DS), about 7 cm from the center of the plasma zone. The substrates for film deposition were placed 1.5 cm further downstream from the DS inlet.

PECVD films were deposited directly on potassium bromide (KBr) disks for FTIR analysis, which was performed on a Perkin Elmer Spectrum 2000 FTIR spectrometer in the transmission mode, with a scanning range of 400 to 4000  $cm^{-1}$  in 1  $cm^{-1}$  increments.

For both XPS and spectroscopic ellipsometry measurements, the PECVD films were deposited on 5 cm diameter silicon wafers. The XPS analysis was carried out in a Surface Science Instruments M-Probe using monochromatic Al  $K\alpha$  X-rays. The surface composition and component atomic ratios were measured from survey scans taken with an analyzer pass energy of 150 eV, and X-ray power of 200 W. Measurements were also taken for individual components' line-shapes, such as C 1s, at a pass energy of 100 eV (higher energy resolution) in order to distinguish between chemistries related to different species in the films. A low energy electron flood source was used to reduce and stabilize electrical charging during analysis [16]. The ellipsometry measurements were carried out with a Woollam variable-angle spectroscopic ellipsometry system with detailed procedures reported elsewhere [14].

For the dielectric and electrical property examinations, the PECVD films were deposited either on 8  $\mu m$  thick polyester (Mylar™) substrate films with one surface coated with 20 nm ( $\pm 3$  nm) thick Al, or 25  $\mu m$  Mylar™ substrate films with both surfaces coated with 20 nm ( $\pm 3$  nm) thick Al, both supplied by Steinerfilm, Inc. After the PECVD film deposition, another Al layer (50 nm  $\pm$  5 nm) was sputtered onto the surface of the PECVD films to make a metal–insulator–metal (M–I–M) sandwich structure for all the dielectric/electrical measurements. The whole preparation process of the M–I–M components was performed in a standard clean room (Class 10,000). The loss factor and the capacitance as well as the derived dielectric constant of the metallized PECVD films were measured with a 4284A precision LCR Meter (Agilent Technologies) in the range of 20 Hz to 1 MHz. The dielectric breakdown strength of the PECVD thin films is defined as the maximum electric field strength that the films can withstand intrinsically without experiencing failure of their insulating properties. In our experiment, the dielectric strength of the films was evaluated using a precision-regulated high voltage power supply (Model 210-05R, Bertran, or Model SR6, Spellman) by gradually increasing the voltage and monitoring the current variation through the films. The voltage was increased in 5 V steps and the duration of each step was 5 s. The breakdown threshold was set at a DC current of  $10^{-7}$  A (the corresponding resistance reading,  $10^8 \sim 10^9$   $\Omega$ , was also used as a reference). For high strength films, 10 V/step was also tested, but no significant difference was observed. All the dielectric properties were measured under ambient conditions with a temperature of  $21 \pm 1.5$  °C and humidity in the range of 50 to 70%.

### 3. Results and discussion

#### 3.1. Plasma polymerized film composition and structure

##### 3.1.1. PP-benzene films

As seen in Fig. 2, the FTIR spectra of all four PP-benzene films show distinct aromatic features including bands in the 3000–3100  $\text{cm}^{-1}$  region corresponding to aromatic C–H stretching and a band at 1030  $\text{cm}^{-1}$  due to C–H in-plane deformation of the benzene ring. Bands at 699 and 750  $\text{cm}^{-1}$  assigned to aromatic ring rocking motion and aromatic C–H out of plane bending, respectively, indicate the formation of monosubstituted benzene rings in the films [17–19]. This is particularly true of the two films prepared in the low pressure regime. Furthermore, small bands in the region of 700 to 900  $\text{cm}^{-1}$  represent the vibrations consistent with a mixture of *m*-, *p*-, and *o*-linked rings and indicate the presence of various substituted aromatic moieties [20,21]. The peaks at 1494 and 1599  $\text{cm}^{-1}$  are assigned to C=C stretching in the aromatic ring and substituted phenyls, as well as to non-conjugated C=C stretching caused by ring opening upon plasma polymerization [22].

Other prominent characteristics presented in the IR spectra of all the PP-benzene films are vibrations from aliphatic structural moieties. The peak at 2867  $\text{cm}^{-1}$  is due to CH<sub>2</sub> and CH stretchings, and the peak at 2955  $\text{cm}^{-1}$  is caused by CH<sub>3</sub> asymmetric stretching. The band at 1452  $\text{cm}^{-1}$  denotes the overlap of CH<sub>3</sub> asymmetric deformation and CH<sub>2</sub> scissoring deformation. There is a marked increase in the intensities of these aliphatic hydrocarbon bands in the high pressure films. The H-PZ film contains many –CH<sub>3</sub> terminal groups, shown by the strong growth in the bands at 2955 and 1452  $\text{cm}^{-1}$  and a new peak which emerges near 1365  $\text{cm}^{-1}$  due to –CH<sub>3</sub> symmetric deformation [23], whereas the H-DS film has a relatively high proportion of –CH<sub>2</sub> and –CH groups. This implies that the H-PZ film has a branched, fragmented structure while the H-DS film has a highly cross-linked structure.

The aromatic character of the PP-benzene films, revealed by IR, was also confirmed by the XPS measurements. In the XPS C

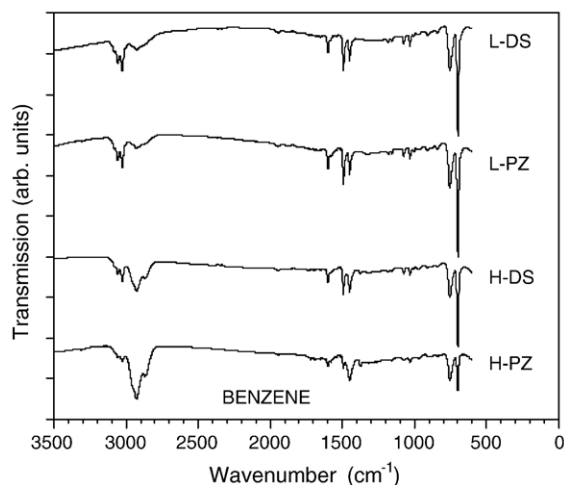


Fig. 2. FTIR spectra of the four PP-benzene films (L-DS, L-PZ, H-DS, and H-PZ).

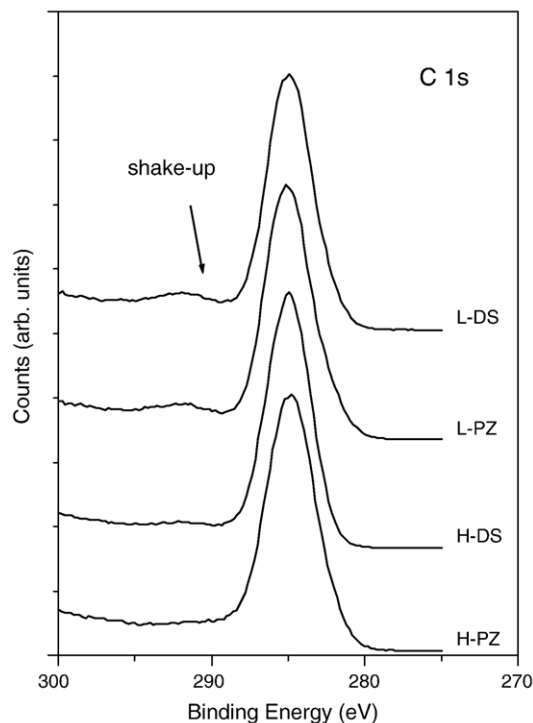


Fig. 3. C 1s photoelectron spectra of the PP-benzene films, showing a shake-up peak near 292 eV arising from the aromatic structure. The films processed in the low pressure regime exhibit a high concentration of aromatic moieties compared to that of the films prepared under high pressure conditions.

1s photoelectron spectra of the four PP-benzene films (seen in Fig. 3), there is a shake-up peak near 292 eV arising from an inelastic loss process that excites the ground-state aromatic ring  $\pi$  orbitals in the polymer ( $\pi \rightarrow \pi^*$ ). This is considered typical for polymers with a significant degree of aromaticity [24]. XPS shows that the L-DS PP-benzene film retains the highest concentration of aromaticity, followed by the L-PZ and H-DS films, with the H-PZ film containing the least, in agreement with the FTIR results.

This structural feature indicates that during the plasma polymerization, the collision frequency and collision cross-section between benzene molecules and activated species had a significant effect on the initiation of the monomer. The initiation of benzene molecules occurs via two different mechanisms depending largely on the residence time. The first type produces activated aromatic radicals by opening the double bonds in the benzene ring due to its relatively low bond dissociation energy (2.74 eV) [16]. The second type is the break-up of the entire benzene ring into many small-molecular alkyl and/or alkenyl radicals (including breaking C–H bonds). For the low pressure cases, a limited residence time led to low collision frequency and collision cross-section [3,25], which would result in single-collision events and the formation of a large quantity of the mono- and multi-substituted aromatic moieties. Under high pressure conditions, where the residence times are longer, the increased collision frequency and cross-section would yield multi-collision events to form a relatively high concentration of alkyl and alkenyl moieties.

It is interesting to note that the film deposition rates in the low pressure regime were much higher,  $105 \pm 9.7$  and  $101 \pm 8.3$  nm/min for the L-PZ and the L-DS films than  $26 \pm 1.5$  and  $21 \pm 1.9$  nm/min for the H-PZ and H-DS films, respectively. Two factors could be the primary causes for this phenomenon. Heavy deposition was observed on the glass wall close to the plasma zone (before downstream) for the high pressure depositions. A large number of activated species were thus consumed before reaching the substrate resulting in an apparent low deposition rate at the substrate. Second, for the low pressure depositions, the large amounts of mono-substituted aromatic species resulted in a relatively loose packing density upon deposition (yielding thicker films). This was confirmed by overnight film immersion tests in acetone where both L-DS and L-PZ films produced substantial fragments which detached from the silicon substrates. Films prepared in the high pressure regime were found not to dissolve.

In addition, a small broad peak in the  $1600\text{--}1700\text{ cm}^{-1}$  range can be assigned to the C=O stretch mode, which suggests that oxygen has been incorporated in these films, especially on film surfaces after exposure to air [26]. Also there is a small shoulder in the region of  $3300\text{--}3400\text{ cm}^{-1}$  (especially for the H-PZ film, shown in Fig. 2), indicating the existence of hydroxyl groups. This was also corroborated by XPS data, which show that the L-DS and L-PZ films contained approximately 2.9 and 3.3 at.% oxygen, whereas the H-DS and H-PZ films contained about 4.1 and 6.8 at.% oxygen, respectively. It seems that the long residence times coupled to the probable collision with higher energy species (in the PZ area) results in the formation of many oxygen-containing centers [27].

### 3.1.2. PP-OFCB films

In Fig. 4, the FTIR spectra of all four PP-OFCB films show strong absorption in the range of  $980\text{--}1450\text{ cm}^{-1}$  due to a convolution of  $(C_mF_n)_x$  vibration modes. The peak located at  $740\text{ cm}^{-1}$  is produced by vibrations from amorphous fluoromoiety [28]. The lack of any distinction between the vibration modes of the various fluorine species and the formation of different bands from a variety of F-containing moieties suggest

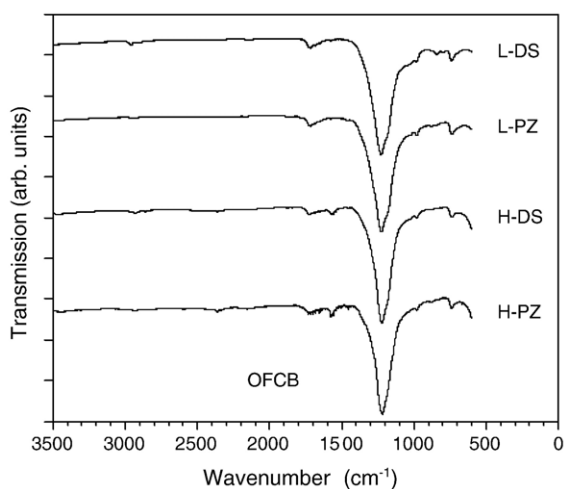


Fig. 4. FTIR spectra of the four PP-OFCB films (L-DS, L-PZ, H-DS, and H-PZ).

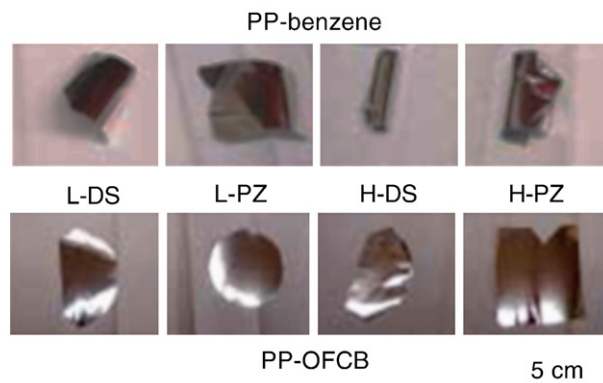


Fig. 5. Photographs of all PECVD films deposited on Al coated Mylar films showing the degree of curling.

the films are somewhat non-descript in composition. There is a small broad peak in the  $1720\text{ cm}^{-1}$  region, possibly due to vibrations of the absorption of C=O and the unsaturated fluorine moieties such as  $C=CF_n$ . However, the XPS data indicates that all PP-OFCB films contain less than 0.4 at.% oxygen, most likely due to surface absorption [29]. The presence of unsaturated fluorine structural units implies that the degree of crosslinking is relatively low [30]. This is confirmed by overnight acetone soaking tests where a considerable portion of the film dissolved. The small molecular materials dissolved could be fluorine-based oligomers.

The structural similarities suggested by FTIR are confirmed by XPS analysis. Atomic compositional analysis indicated  $\sim 40$  at.% carbon and  $\sim 60$  at.% fluorine, except for the H-PZ film which had a slightly lower fluorine concentration. Hydrogen is not detected in XPS. The high F/C ratio of the OFCB monomer (F/C=2:1) compared to the PP-OFCB films (F/C=approximately 1.5:1) indicates that defluorination takes place during the plasma reactions, presumably through C–F bond cleavage which influences the formation of a branched structure [16,31]. A weak vibration band at  $2950\text{ cm}^{-1}$  indicates the incorporation of hydrogen as aliphatic structural units in the final PECVD films. The hydrogen must originate from interactions with residual moisture in the chamber and/or sputtering from old deposits on the wall of the reaction chamber since no H is present in the monomer. The deposition rates are  $11.2 \pm 1.0$ ,  $7.8 \pm 0.73$ ,  $5.8 \pm 0.51$ , and  $4.1 \pm 0.33$  nm/min for the L-PZ, L-DS, H-PZ, and H-DS films, respectively. These deposition rates were much lower than those of the corresponding PP-benzene films.

Curling of the Al-coated Mylar films after PECVD deposition can be used as a qualitative measure of film crosslink density. Curling is caused by internal stresses in the PP-films which arise from reactive plasma species that continuously impinge onto the film during growth [32]. Generally, the internal stress has been shown to depend on the degree of crosslinking [1,33], with higher crosslink densities leading to higher internal stresses. Fig. 5 shows photographs of all PECVD samples indicating much stronger curling in the PP-benzene films, especially for the H-DS film. However, the PP-OFCB films showed rather limited propensity to curl. These results are in qualitative agreement with the film immersion studies described above.

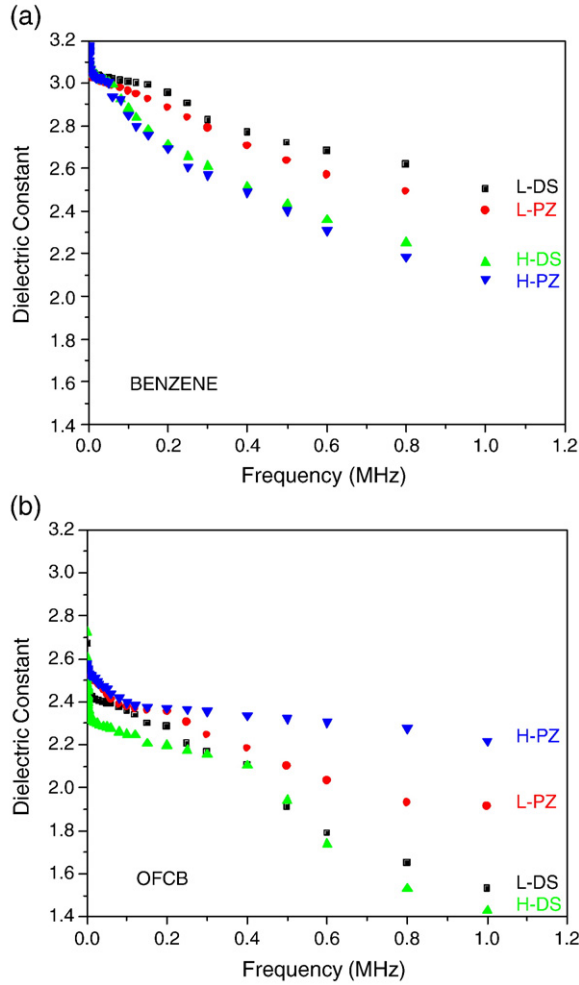


Fig. 6. The dependence of dielectric constant ( $\epsilon$ ) with frequency for: (a) the four PP-benzene films, and (b) the four PP-OFCB films (L-DS, L-PZ, H-DS, and H-PZ).

### 3.2. Dielectric properties of the PECVD films

#### 3.2.1. PP-benzene films

Fig. 6a shows the variation of dielectric constant,  $\epsilon_r$ , with frequency, for all four PP-benzene films. The dielectric constants at 1 kHz were 3.06, 3.06, 3.07 and 3.11 for the L-DS, L-PZ, H-DS, and H-PZ PP-benzene films, respectively. These are higher than those of conventional polymers including polyethylene, polypropylene and polystyrene [34]. Fig. 6a also indicates a gradual decrease of the dielectric constant with increasing frequency after an initial sharp drop at low frequencies. For polymer materials, the dielectric constant or relative permittivity,  $\epsilon_r$ , is composed of three components as shown in Eq. (1):

$$\epsilon_r = \epsilon_{\text{electronic}} + \epsilon_{\text{ionic}} + \epsilon_{\text{orientational}} \quad (1)$$

Both the dielectric constant,  $\epsilon_r$ , and the optical refractive index,  $n$ , can be used to describe the polarizability of matter and are related by the following equation:

$$\epsilon_r = n^2 \quad (2)$$

At high frequencies, only the electrons can follow the variation of the applied field so the only contribution to the dielectric constant should be from electronic phenomena. Therefore, Eq. (2) can be simplified as follows.

$$\epsilon_{\text{electronic}} = n^2 \quad (3)$$

For all PP-benzene films, the refractive indices determined by spectroscopic ellipsometry were 1.62–1.63 at 700 nm. This leads to a calculated  $\epsilon_{\text{electronic}}$  of approximately 2.64. The high proportion of  $\epsilon_{\text{electronic}}$  ( $\sim 85\%$ ) to the total  $\epsilon$  indicates that contributions from  $\epsilon_{\text{ionic}}$  and  $\epsilon_{\text{orientational}}$  are low, which can be attributed to the lack of molecular mobility (confined by the crosslinking) and low ionic polarization of the molecular structures [6]. The frequency dependence of  $\epsilon_r$  is indicative of electronic polarization [35] due to oligomers/fragments, polar side groups, and residual free radicals effects on interfacial polarization and microscopic field distortion. The  $\epsilon_r$  of high pressure PP-benzene films had a more pronounced frequency dependence than the films prepared in the low pressure regime. The PZ films also exhibit a stronger decrease in  $\epsilon_r$

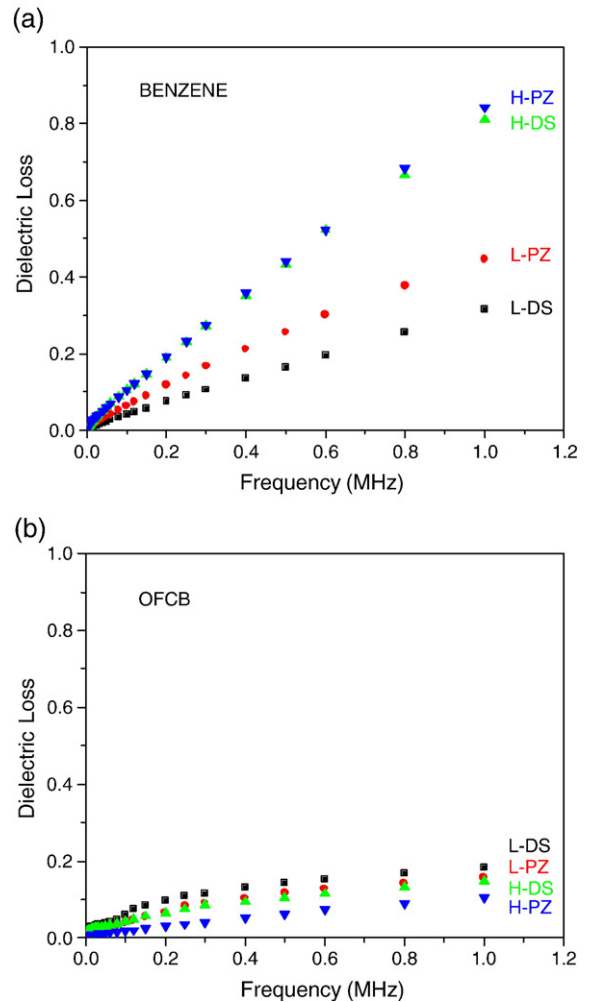


Fig. 7. The dependence of dielectric loss,  $\tan \delta$  with frequency for: (a) the four PP-benzene films, and (b) the four PP-OFCB films (L-DS, L-PZ, H-DS, and H-PZ).

with frequency than the corresponding DS films. These differences are due to the high oxygen content and the contribution of the C=O groups at the film surfaces [36]. These polar surface groups can reorient more easily at the surface than in the bulk. The initial sharp decrease in dielectric constant at low frequencies can be traced to orientational polarizations of trapped free radicals, unpaired electron sites, oligomeric structures, and polar groups under an applied external electrical field [6].

Dielectric loss,  $\tan \delta$ , is an important characteristic, which indicates the dissipation of energy due to the exponential decay of polarization with time in a dielectric material once the applied field is removed. Measured dielectric losses at 1 kHz were close, ranging from  $5.2\text{--}8.7 \times 10^{-3}$  as seen in Fig. 7a. In general, these PECVD polymer films have slightly higher dielectric loss values due to plasma damage incurred during film growth [37]. An apparent increase in  $\tan \delta$  with increasing applied frequency is dominated by resistive losses since the mobile charges contained in the film cannot follow higher frequency electric fields. This loss of energy is associated with the degree of orientation of molecules in addition to the degree of internal friction of the polymer [37]. Since PP-benzene films are strongly crosslinked, the polymer backbones have limited molecular mobility. The increase in  $\tan \delta$  with frequency can then be attributed to the introduction of polar impurities in the PP-benzene polymers [38].

### 3.2.2. PP-OFCB

Similar to PP-benzene films, the dielectric constant of the PP-OFCB films is mainly determined by the electronic polarization. Measured dielectric constants at 1 kHz of 2.41, 2.52, 2.42, and 2.54 for L-DS, L-PZ, H-DS, and H-PZ, respectively, are shown in Fig. 6b. The measured refractive index at 700 nm is approximately 1.38 for the four PP-OFCB films. The calculated value of  $\epsilon_{\text{electronic}}$  of 1.9 again indicates a major contribution to the total  $\epsilon$  from electronic polarization ( $\sim 75\%$ ). The dielectric constant of these PP-OFCB films is higher than that of Teflon<sup>TM</sup> (2.1) or bulk poly(tetrafluoroethylene) PTFE films (around 2–2.2) [27], an analogous linear polymer, indicating some contributions from ionic and orientation polarizations. The slightly lower contribution from the  $\epsilon_{\text{electronic}}$  for the PP-OFCB films ( $\sim 75\%$ ) than for the PP-benzene films ( $\sim 85\%$ ) supports the previous conclusion that the degree of crosslinking is lower than in the corresponding PP-benzene films.

Unlike the dielectric constant of conventional, linear PTFE polymers which do not show significant frequency dependence because of the presence of symmetrical dipoles in the structure, there is a distinct frequency dependence of the dielectric constant for PP-OFCB films as shown in Fig. 6b. At high frequencies, the decrease in  $\epsilon_r$  is due to incomplete dielectric relaxation [39].

Unlike the PP-benzene films, oxygen cannot be a key factor in affecting  $\epsilon_r$  since there is very little, if any, oxygen in the films. Therefore, the contributions from both orientational and ionic polarizations could include those from the presence of asymmetric moieties including CF–CF<sub>2</sub>–CF<sub>3</sub>, CF<sub>2</sub>–CF<sub>2</sub>–CF<sub>3</sub>, CF<sub>2</sub>–CH<sub>2</sub> and unsaturated species, such as –C=CF<sub>2</sub>, –CF=CF<sub>2</sub>, and –CF=CF–.

The values of dielectric loss, at 1 kHz ranged from  $4.3\text{--}5.9 \times 10^{-3}$  as seen in Fig. 7b. These are more than an order of magnitude higher than conventional bulk PTFE (around  $2 \times 10^{-4}$ ) [27]. The dielectric loss of the PP-OFCB films increases only slightly with frequency, and very little difference between the films is observed. Again, this is attributable to fundamental differences in film structures between the linear PTFE and the amorphous, cross-linked structures of PP-OFCB films, which also contain asymmetric and unsaturated fluorocarbon moieties, oligomers and fragments, and trapped free radicals.

### 3.3. Breakdown strength of the PECVD films

Table 1 lists the average breakdown strength,  $F_b$ , of all films. More than 10 testing points were chosen for each sample, and the listed  $F_b$ 's are the mean values of the experimental data. The thicknesses of the tested films were in the range of 0.6 to 1.2  $\mu\text{m}$ . No significant thickness effect was observed on the dielectric constant and dielectric loss data. Also, our preliminary results demonstrated that measurements of the M-I-M samples with asymmetric electrodes did not show any apparent differences in characteristics with alteration of the polarity of applied voltage. A self-healing phenomenon for some of the deposited films was observed. Only the breakdown strength without the self-healing phenomenon is reported here. In general, the PP-benzene films exhibit higher breakdown strengths and the average  $F_b$  for all PP-benzene films is greater than 300 V/ $\mu\text{m}$ . Fig. 8 shows typical breakdown (voltage–current) curves from the H-DS and H-PZ PP-benzene films, displaying that when the voltage exceeds the maximum sustainable electrostatic field across the tested films, a catastrophic breakdown occurs, causing a drastic increase in current. In this test, the H-DS PP-benzene film exhibits an  $F_b$  of 676 V/ $\mu\text{m}$  ( $=500/0.74$ ), and that of the H-PZ PP-benzene film, 380 V/ $\mu\text{m}$  ( $=350/0.92$ ). Among all the PECVD films, the H-DS PP-benzene exhibits the highest average  $F_b$ , 610 V/ $\mu\text{m}$ . The PP-OFCB films had  $F_b$  values near 200 V/ $\mu\text{m}$ , except for the H-PZ film with a measured  $F_b$  of 325 V/ $\mu\text{m}$ .

The dielectric strength of polymeric films is dependent on a number of structural characteristics being closely associated with the packing density of the materials, including the polarity, dimension, and steric structure of the molecules and/or molecular building blocks. The high average breakdown

Table 1

Average breakdown strength ( $F_b$ ) of the PECVD films\*

Materials	L-PZ Benzene	L-DS Benzene	H-PZ Benzene	H-DS Benzene	L-PZ OFCB	L-DS OFCB	H-PZ OFCB	H-DS OFCB
$F_b$ (V/ $\mu\text{m}$ )	334 $\pm$ 54	323 $\pm$ 57	380 $\pm$ 59	610 $\pm$ 57	226 $\pm$ 41	201 $\pm$ 50	325 $\pm$ 49	199 $\pm$ 19

\* Film thickness is in the range of 0.6 to 1.2  $\mu\text{m}$ . L: films prepared in the low pressure regime (6.7 Pa); H: films prepared in the high pressure regime (80 Pa); PZ: monomer fed into the plasma zone; DS: monomer fed into the downstream region.

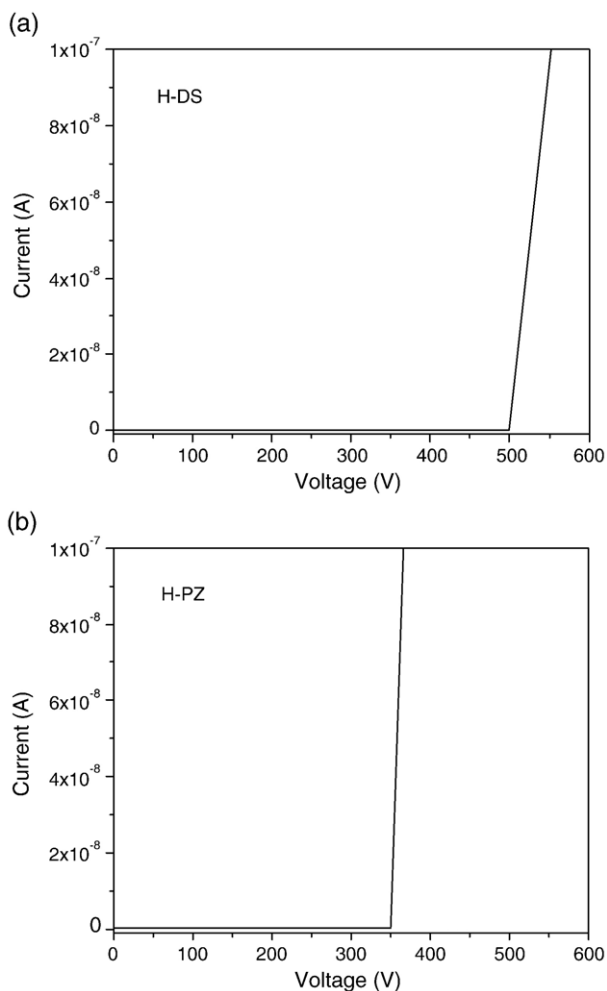


Fig. 8. Typical current–voltage ( $I$ – $V$ ) diagrams of the breakdown strength measurements of the H-DS and H-PZ PP-benzene films. The thickness of the H-DS film was  $0.74\ \mu\text{m}$  and the thickness of the H-PZ film was  $0.92\ \mu\text{m}$ .

strength ( $610\ \text{V}/\mu\text{m}$ ) for the H-DS PP-benzene film is remarkable. We speculate that the high chamber pressure provides a long species residence time, which leads to a high collision cross section for the benzene precursors. The downstream monomer feeding location provides meta-stable argon molecules with  $12.5\ \text{eV}$  energy, large enough to excite the easy-to-initiate benzene molecules, but is far enough away to avoid many harmful side reactions present in the plasma zone feed location. The combination of this high pressure regime and downstream feed location offers a suitable reaction environment for the benzene molecules to create a relatively high concentration of small molecular activated species with mostly aliphatic CH and  $\text{CH}_2$  moieties, promoting the formation of a highly crosslinked structure.

Bulk PTFE with an  $F_b$  of  $110\ \text{V}/\mu\text{m}$  [40] exhibits only about half the  $F_b$  values of PP-OFCB films. The lower dielectric strengths observed for PP-OFCB films are attributed to the less-densely crosslinked structures. During plasma polymerization, micro-pores and thus higher free volume is introduced into the bulk structure of the PP-OFCB films due to the larger fluorine atom dimension [41,42]. The high breakdown strength ( $325\ \text{V}/$

$\mu\text{m}$ ) measured for the H-PZ PP-OFCB film relative to the other PP-OFCB films is due to the combination of the high pressure regime and plasma zone feeding mode. For the difficult-to-initiate OFCB molecules, the vigorous PZ reaction environment plus the long residence time result in a high collision cross section which produces relatively large quantities of reactive carbon and fluorine species.

#### 4. Conclusions

PECVD can be utilized to fabricate high breakdown strength dielectric polymer films. Different organic precursors can be utilized and by adjusting the deposition conditions, the final film structure and resulting properties can be manipulated. Two important variable deposition conditions include the pressure within the reactor and the monomer feed location relative to the plasma zone. Plasma deposited films from both benzene and OFCB were characterized.

Films deposited under the optimum conditions exhibit a highly crosslinked structure. These films exhibit higher dielectric constants than corresponding conventional polymer materials. The bulk of the contribution is electronic. The small sharp drop in  $\epsilon_r$  at low frequencies can primarily be attributed to some orientational polarization caused by the presence of trapped free radicals or the formation of polar/oxygenated groups. While the measured dielectric loss of the PECVD films is comparable to many conventional polymer materials at  $1\ \text{kHz}$ , a continuous decrease in dielectric constant and a significant increase in the dielectric loss as a function of applied frequency are observed. It appears that the  $\text{C}=\text{O}$  polar content plays a dominant part in affecting the frequency dependences of both  $\epsilon$  and  $\tan\delta$  for the PP-benzene films.

Finally, the film crosslink density of the PECVD plays a key role in determining the breakdown strength. PP-benzene films have high average  $F_b$  values compared to the PP-OFCB films, with the highest value of  $610\ \text{V}/\mu\text{m}$ . Among the PP-benzene films, those fabricated in the low pressure regime had lower  $F_b$  values than those prepared in the high pressure regime, presumably due to the presence of a large number of randomly aligned aromatic moieties leading to a lower film packing density. Since the OFCB molecules are more difficult in terms of reaction initiation, the plasma zone reaction conditions and high pressure environment for the H-PZ films combine to form PP-OFCB films with higher crosslinking density, resulting in a high breakdown strength ( $325\ \text{V}/\mu\text{m}$ ) compared to the other PP-OFCB films.

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#### References

- [1] H. Yasuda, Plasma Polymerization, Academic Press, Orlando, FL, 1985.
- [2] R. d'Agostino (Ed.), Plasma Deposition, Treatment, and Etching of Polymers, Academic Press, San Diego, 1990.

- [3] H. Biederman, Y. Osada, Plasma Polymerization Processes, Elsevier, Amsterdam, 1992.
- [4] N. Inagaki, Plasma Surface Modification and Plasma Polymerization, Technomic Publishing Company, Inc., Lancaster, PA, 1996.
- [5] M.S. Silverstein, I. Visoly, O. Kesler, M. Janai, Y. Cassuto, J. Vac. Sci. Technol., B 16 (1998) 2957.
- [6] K. Endo, K. Shinoda, T. Tatsumi, J. Appl. Phys. 86 (1999) 2739.
- [7] S.-H. Cho, Z.-T. Park, J.-G. Kim, J.-H. Boo, Surf. Coat. Technol. 174–175 (2003) 1111.
- [8] H. Biederman, Plasma Polymer Films, Imperial College Press, London, 2004.
- [9] H.V. Boenig, Fundamentals of Plasma Chemistry and Technology, Technomic Publishing, Lancaster, PA, 1988.
- [10] C.J. Drummond, Z.R. Vasic, N. Geddes, M.C. Jurich, R.C. Chatelier, T.R. Gengenbach, H.J. Griesser, Colloids Surf., A Physicochem. Eng. Asp. 129–130 (1997) 117.
- [11] B. Mitu, S. Bauer-Gogonea, H. Leonhartsberger, M. Lindner, S. Bauer, G.B. Dinescu, Surf. Coat. Technol. 174–175 (2003) 124.
- [12] D.S. Kumar, Y. Yoshida, Surf. Coat. Technol. 169/170 (2003) 600.
- [13] I.-S. Bae, S.-H. Cho, Y.S. Park, B. Hong, Z.T. Park, J.-G. Kim, J.H. Boo, Thin Solid Films 506/507 (2006) 2.
- [14] H. Jiang, W.E. Johnson, J.T. Grant, K. Eyink, E.M. Johnson, D.W. Tomlin, T.J. Bunning, Chem. Mater. 15 (2003) 340.
- [15] H. Jiang, K. O'Neill, J.T. Grant, S. Tullis, K. Eyink, W.E. Johnson, P. Fleitz, T. Bunning, Chem. Mater. 16 (2004) 1292.
- [16] H. Jiang, J.D. Grant, S. Tullis, K. Eyink, P. Fleitz, T.J. Bunning, Polymer 45 (2004) 8475.
- [17] K. Jesch, J.E. Bloor, P.L. Kronick, J. Polym. Sci., A 14 (1966) 1487.
- [18] J.M. Tibbitt, M. Shen, A.T. Bell, J. Macromol. Sci., Part A, Pure Appl. Chem. 10 (1976) 1623.
- [19] A. Joshi, S.A. Gangal, S.K. Kulkarni, J. Appl. Phys. 64 (1988) 6668.
- [20] I. Retzko, J.F. Friedrich, A. Lippitz, W.E.S. Unger, J. Electron Spectrosc. Relat. Phenom. 121 (2001) 111.
- [21] S.F. Durrant, R.P. Mota, M.A.B. de Moraes, Thin Solid Films 220 (1992) 295.
- [22] R.M. Silverstein, F.X. Webster, Spectrometric Identification of Organic Compounds, John Wiley and Sons, New York, 1998.
- [23] R. Magno, J.G. Adler, Thin Solid Films 42 (1977) 237.
- [24] G. Beamson, D. Briggs, High Resolution XPS of Organic Polymers, Wiley, New York, 1992.
- [25] M. Duval, A. Theoret, J. Appl. Polym. Sci. 17 (1973) 527.
- [26] J.T. Grant, H. Jiang, S. Tullis, W.E. Johnson, K. Eyink, P. Fleitz, T.J. Bunning, Vacuum 80 (2005) 12.
- [27] H. Biederman, Thin Solid Films 86 (1981) 125.
- [28] W. De Wilde, Thin Solid Films 24 (1974) 101.
- [29] H. Biederman, Y. Osada, Advances in Polymer Science, vol. 95, Springer-Verlag, Berlin, 1990, p. 57.
- [30] S. Agraharam, D.W. Hess, P.A. Kohl, S.A. Bidstrup Allen, J. Vac. Sci. Technol., B 19 (2001) 439.
- [31] H. Jiang, J.T. Grant, K. Eyink, S. Tullis, J. Enlow, T.J. Bunning, Polymer 46 (2005) 8178.
- [32] L. Zuri, M. Narkis, M.S. Silverstein, Polym. Eng. Sci. 37 (1997) 1188.
- [33] A. Morinaka, Y. Asano, J. Appl. Polym. Sci. 27 (1982) 2139.
- [34] J.I. Kroschwitz (Ed.), Electrical and Electronic Properties of Polymers: A State-of-the-Art Compendium, John Wiley & Sons, New York, 1988.
- [35] A. von Hippel, E.P. Gross, J.G. Jelatis, M. Geller, Phys. Rev. 91 (1953) 568.
- [36] J.T. Grant, H. Jiang, K. O'Neill, K. Eyink, W. Johnson, E.M. Johnson, S. Tullis, D.W. Tomlin, P. Fleitz, T.J. Bunning, Mater. Technol. 38 (2004) 3.
- [37] C. Biloiu, I.A. Biloiu, Y. Sakai, H. Sugawara, A. Ohta, J. Vac. Sci. Technol., A 22 (2004) 1158.
- [38] S.D. Phadke, Thin Solid Films 48 (1978) 319.
- [39] L.M. Han, R.B. Timmons, W.W. Lee, J. Vac. Sci. Technol., B 18 (2000) 799.
- [40] I.H. Pratt, T.C. Lausman, Thin Solid Films 10 (1972) 151.
- [41] T. Nakano, M. Fukuyama, H. Hayashi, K. Ishii, Y. Ohki, IEEE Trans. Electr. Insul. 25 (1990) 1085.
- [42] K. Hozumi, in: C.J. Timmermans (Ed.), Proceedings of the 7th International Symposium on Plasma Chemistry, Eindhoven, the Netherlands, July 1–5 1985, p. 1284.