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**THE STRUCTURE AND DIELECTRIC PROPERTIES OF
PLASMA-POLYMERIZED BENZENE AND OFCB THIN
FILMS (PREPRINT)**

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**Hardened Materials Branch
Survivability and Sensor Materials Division**

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14. ABSTRACT Polymeric dielectric and photonic thin films can be fabricated using plasma enhanced chemical vapor deposition (PECVD), a room temperature, solvent-free and versatile technique. Many organic precursors have been deposited yielding plasma polymerized thin films with a wide range of functionalities. These films, exhibiting highly cross-linked structures, pin-hole free bulk morphologies and smooth surfaces for a variety of film thicknesses, have been targeted for optical and dielectric applications such as waveguides, AR coatings, band-gap filters for integrated optics, and high performance dielectric devices. In this work, benzene and octafluorocyclobutane (OFCB) were chosen as starting precursors for exploring the relationship between structure and dielectric properties.					
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The structure and dielectric properties of plasma-polymerized benzene and OFCB thin films

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Introduction

Polymeric dielectric and photonic thin films can be fabricated using plasma enhanced chemical vapor deposition (PECVD), a room temperature, solvent-free and versatile technique. Many organic precursors have been deposited yielding plasma polymerized thin films with a wide range of functionalities. These films, exhibiting highly cross-linked structures, pin-hole free bulk morphologies and smooth surfaces for a variety of film thicknesses, have been targeted for optical and dielectric applications such as waveguides, AR coatings, band-gap filters for integrated optics, and high performance dielectric devices. In this work, benzene and octafluorocyclobutane (OFCB) were chosen as starting precursors for exploring the relationship between structure and dielectric properties.

Experimental

Figure 1 is a schematic of the PECVD set-up. Briefly, 99.999% argon was used as a noble gas flowing into a 10 cm diameter glass reactor through a capacitively coupled, 13.56 MHz discharge. Two precursors were chosen: benzene (C₆H₆, Aldrich, liquid, HPLC grade, purity > 99.9%) and octafluorocyclobutane (C₄F₈, OFCB, SynQuest Laboratories, compressed gas, purity > 99%), used as received. For OFCB, the flow rate was controlled in the range of 0.5 - 3 cc/min, and for benzene, vapor flow rate in the range of 0.05 - 0.3 cc/min. Two reaction chamber pressures, 0.05 torr as the low pressure regime (L-), and 0.6 torr as the high pressure regime (H-) were used. A plasma power of 45W and argon flow rates of 20 cc/min (for the L) or 100 cc/min (for the H) were utilized. The monomer feed location was set either at the center of the plasma zone (PZ) or at 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.

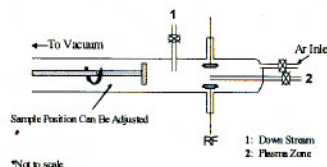


Figure 1. A schematic of the PECVD set-up

Plasma polymerized (PP) films were deposited directly on potassium bromide (KBr) disks for FTIR analysis, performed on a Perkin Elmer Spectrum 2000 FT-IR spectrometer in the transmission mode. For both XPS and spectroscopic ellipsometry measurements, the PP-films were deposited on 2" silicon wafers. The XPS analysis was carried out in a Surface Science Instruments M-Probe using monochromatic Al K α x-rays. The surface composition and component atomic ratios were measured from survey scans taken in order to distinguish between chemistries related to the formation of different species in the films. The ellipsometry measurements were carried out with a Woollam variable-angle spectroscopic ellipsometry system.

For the dielectric and electrical property examinations, the PP-films were deposited either on 8 μ m thick polyester (MylarTM) substrate with one surface coated with 20 nm thick Al or 25 μ m MylarTM substrates with both surfaces coated with 20 nm thick Al, supplied by Steinerfilm. After the PP-film deposition, another Al layer (50 nm) was evaporated onto the surface of the PP-films to form an M-I-M sandwich structure for the dielectric/electrical measurements. The loss factor, the capacitance and the derived dielectric constant were measured with a 4284A precision LCR Meter (Agilent Technologies) in the range of 20 Hz to 1 MHz. The breakdown strength was evaluated using a precision-regulated high voltage power supply (Model 210-05R, Bertran).

Results and Discussion

PECVD film structure and composition

1. PP-benzene films

As seen in Figure 2a, the FTIR spectra of all four PP-benzene films show distinct aromatic characteristics such as bands in the 3000 - 3100 cm⁻¹ region, at 1030, 750, and 699 cm⁻¹. Small bands in the region of 700 to 900 cm⁻¹ represent the vibrations consistent with a mixture of *m*-, *p*-, and *o*-linked rings. This feature was confirmed by a shake-up peak near 292 eV in the XPS C 1s photoemission spectra arising from an inelastic loss process that excites the ground-state aromatic ring orbitals in the films ($\pi \rightarrow \pi^*$). Another prominent trait is vibrations from aliphatic moieties, including a peak at 2867 cm⁻¹ due to CH₂ and CH stretchings, a peak at 2955 cm⁻¹ caused by CH₃ asymmetric stretching and a band at 1452 cm⁻¹ denoting the overlap of CH₃ asymmetric deformation and CH₂ scissoring deformation. A marked increase in the intensities of the C-H bands is present for the high pressure films. Furthermore, a small peak in the 1600-1700 cm⁻¹ range, assigned to the C=O stretch mode, suggests oxygen incorporation in these films. This was 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 4.1 and 6.8 at% oxygen, respectively.

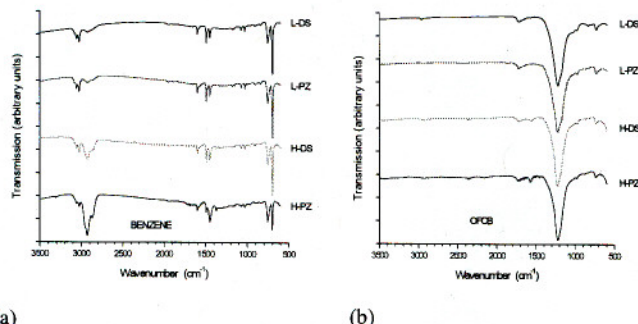


Figure 2. IR-Spectra of: (a) four PP-Benzene films, L-DS, L-PZ, H-DS, H-PZ; (b) four PP-OFCB films, L-DS, L-PZ, H-DS, H-PZ.

2. PP-OFCB films

Figure 2b, the FTIR spectra of all four PP-OFCB films, shows strong absorption in the range of 980 to 1450 cm⁻¹ due to a convolution of C_mF_n and (C_mF_n)_x vibration modes. The peak located at 740 cm⁻¹ is produced by vibrations from amorphous fluoro-moieties. The lack of any distinction between the vibration modes of the various fluorine species suggest the films are somewhat non-descript in composition. The presence of unsaturated structural units implies that the degree of crosslinking is relatively low. This is confirmed by overnight acetone soaking tests where a considerable portion of the film dissolved. The small molecular materials dissolved were confirmed to be fluorine-based oligomers using NMR measurements. The XPS data indicates that all PP-OFCB films contain less than 0.4 at% oxygen, most likely due to surface absorption. The structural similarity suggested by FTIR is also confirmed by XPS analysis, indicating carbon (~40 at%) and fluorine (~60 at%) concentrations. 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) implies that defluorination took place during the plasma reactions.

Dielectric Properties of the PECVD films

1. PP-benzene films

Figure 3a shows the variation of dielectric constant, ϵ , 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. A gradual decrease of the dielectric constant with frequency after an initial sharp drop at low frequencies is seen in Figure 2a. The ϵ is composed of three components:

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

where $\epsilon_{\text{electronic}} = n^2$ and n is the optical refractive index of the material. For all PP-benzene films, the refractive indices determined by the 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 $\epsilon_{\text{electronic}}$ (~ 85 %) of the total ϵ indicates that contributions from ϵ_{ionic} and $\epsilon_{\text{orientational}}$ are low, due to lack of molecular mobility (confined by the crosslinking) and low ionic polarization of the molecular structures. The frequency dependence of ϵ is due to the electronic polarization, attributed to oligomers/fragments, polar side groups, and residual free radicals, effects on interfacial polarization and microscopic field distortion, and the initial sharp decrease in ϵ at low frequencies can be traced to orientational polarizations of trapped free radicals and surface polar groups under an applied external electrical field. The ϵ of high pressure PP-benzene films had a more pronounced frequency dependence compared to the films prepared in the low pressure regime. The PZ films also exhibit slightly more decrease in ϵ with frequency than the corresponding DS films. These differences are due to the high oxygen content.

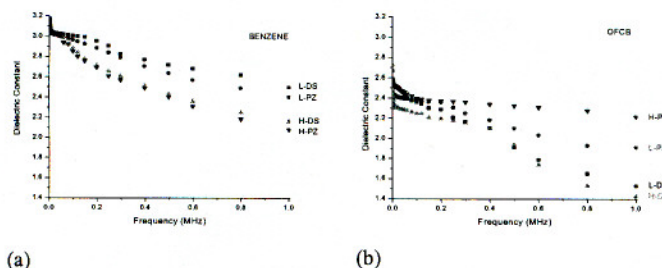


Figure 3. The dependence of dielectric constant (ϵ) with frequency for: (a) four of the PP-benzene films, and (b) four of the PP-OFCB films.

Dielectric loss, $\tan \delta$, 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 - 8.7×10^{-3} as seen in Figure 4a. In general, the PECVD films have slightly higher dielectric loss values due to plasma damage incurred during film growth. 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. PP-benzene films are strongly crosslinked so that their 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 films. Since benzene molecules have a low excitation barrier and are readily initiated during plasma polymerization, 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.

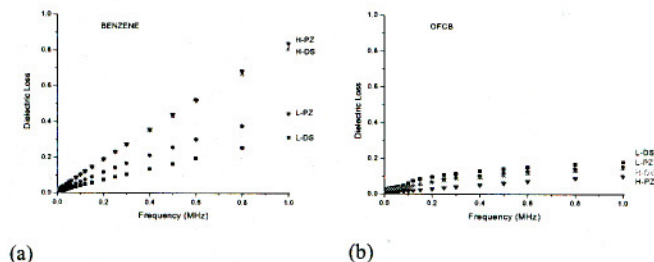


Figure 4. The dependence of dielectric loss, $\tan \delta$, with frequency for: (a) four of the PP-benzene films, and (b) four of the PP-OFCB films.

2. PP-OFCB films

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 2.52, 2.41, 2.54, and 2.42 for L-PZ, L-DS, H-PZ, and H-DS, respectively, are shown in Figure 3b. The measured refractive index at 700 nm is approximately 1.38 for the PP-OFCB films. The calculated value of $\epsilon_{\text{electronic}}$ of 1.9 again indicates a major contribution to the total ϵ from electronic polarization (~ 75 %). The dielectric constant of the PP-OFCB films is higher than that of conventional PTFE (~2.1), an analogous linear polymer, indicating contributions from ionic and orientation polarizations. The slightly lower contribution from the $\epsilon_{\text{electronic}}$ for the PP-OFCB films (~ 75 %) than for the PP-benzene films (~ 85 %) supports the conclusion that the degree of crosslinking is lower than the corresponding PP-benzene films.

Breakdown strength of the PECVD films

Table 1 lists the average breakdown strength, F_b , of all films. In general, the PP-benzene films exhibit the high breakdown strengths, with average F_b greater than 300 V/ μm . The film prepared in the high pressure regime and with the downstream monomer feed location had an highest average F_b of 610 V/ μm . The PP-OFCB films had F_b values near 200 V/ μm , except for the H-PZ film with a measured F_b of 325 V/ μm .

Table 1: Average breakdown strength (F_b) of the PECVD films*

PP-film	L-PZ B	L-DS B	H-PZ B	H-DS B	L-PZ F	L-DS F	H-PZ F	H-DS F
F_b	334 $\pm$	323 $\pm$	380 $\pm$	610 $\pm$	226 $\pm$	201 $\pm$	325 $\pm$	199 $\pm$
V/ μm	53.8	57.8	59.4	57.1	41.4	50.0	49.2	19.0

*B: PP-Benzene; F: PP-OFCB

The dielectric strength of polymeric materials is dependent on a number of structural characteristics including the nature, size, packing density, and polarity of molecules. Bulk PTFE with an F_b of 110 V/ μm exhibits only about half the F_b values of PP-OFCB films. The higher dielectric strengths observed for PP-benzene films are attributed to the densely crosslinked structures. The high average breakdown strength (610 V/ μm) for the H-DS 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 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 these two conditions 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 CH₂ moieties, promoting the formation of a highly crosslinked structure. 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. This, in addition to the low crosslinking density, leads to a low F_b .

Conclusions

Using PECVD techniques, various organic precursors can be polymerized into dense, crosslinked thin films. Adjusting the processing conditions including the monomer feed location and ratio, chamber pressure, and plasma power, allows manipulation of the final film structure and resulting properties. This has been demonstrated here with respect to the fabrication of high performance dielectric films.

The PP-films exhibit higher dielectric constants and breakdown strength than corresponding conventional polymer materials. The bulk of the contribution is electronic. The small sharp drop in ϵ at low frequencies can primarily be attributed to some orientational polarization caused by the trapped free radicals or the formations of polar/oxygenated groups and oligomers. For all of the PP- films, a continuous decrease in dielectric constant and a significant increase in the dielectric loss as a function of applied frequency is observed, especially for the PP-benzene films. It appears that the C=O polar content plays a dominant part in affecting the frequency dependences of both ϵ and $\tan \delta$. However, for the PP-OFCB, the primary cause is due to the relatively low crosslinking.

Finally, the crosslink density of the PECVD films plays a key role in determining the breakdown strength. PP-benzene films have high average F_b compared to the PP-OFCB films, with a highest value of 610 V/ μm .