

# Investigation of Plasma Polymerized Benzene and Furan Thin Films for Application in Opto-electronic Devices

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**ABSTRACT:** Conjugated polymers are among the most promising organic materials for opto-electronic devices. In such applications, the main fabrication problem is to get uniform, defect-free, and reproducible thin films of these materials. In this investigation, an RF plasma reactor was used to produce cross-linked organic thin films from benzene and furan precursors. Uniform thin films of desired thickness were fabricated using this plasma polymerization technique. The composition of the plasma-polymerized films was determined with X-ray photoelectron spectroscopy. Fourier transform infrared spectra of the monomers and plasma-polymerized thin films prepared were compared to analyze the chemical structure of the films. Ultra-

violet-visible absorption spectroscopy shows a red shift of 45 nm in  $\lambda_{\max}$  for the case of plasma-polymerized benzene films and 52 nm in the case of plasma-polymerized furan films when compared to their respective monomer spectra. Photo luminescence spectra of these films show a blue emission with a broad peak at 460 nm for the plasma-polymerized benzene films and 445 nm for the plasma-polymerized furan films. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 523–528, 2003

**Key words:** plasma polymerization; light emission; thin films; optics

## INTRODUCTION

Over the past 15 years or so it has been shown that organic thin films have great potential for use in opto-electronic applications.<sup>1–3</sup> Ever since Tang and Van Slyke<sup>4</sup> first reported a highly efficient light emitting diode (LED) with vacuum deposited organic thin films, there has been a lot of interest in identifying light emitting organic materials. To date, numerous organic materials have been tried<sup>5–8</sup> but the main problem with these materials is to produce uniform, defect-free, and reproducible thin films. Therefore, various synthetic approaches have been directed towards the preparation of soluble precursors or derivatives of these materials that are processable by simple spin coating methods.

The approach adopted here is to use the plasma-enhanced chemical vapor deposition (PECVD) or plasma polymerization technique to prepare optical quality organic thin films. It is well known that plasma polymerization is appropriate for preparing thin films with dense and pinhole-free structures.<sup>9</sup> These films are also very adherent to a variety of substrates, resistant to solvents, and can be produced with a variety of chemical and optical properties.<sup>2,9</sup> Other advantages

of this technique are that multilayered structures can be easily prepared and the use of solvents may be avoided.

In this paper we report the successful fabrication of the organic thin films of benzene and furan by the PECVD technique. Fourier transform infrared (FTIR), X-ray photoelectron spectroscopy (XPS), ellipsometry, and ultraviolet-visible (UV-vis) absorption spectra of these films were recorded to obtain information about the properties of these films. Photoluminescence (PL) spectra of these films show emission in the blue region for both benzene and furan.

## EXPERIMENTAL

### Materials

Benzene and furan were purchased from Aldrich Chemical Company and were used without any further purification. The argon used in the plasma system was High Purified Grade and was supplied by Wright Brothers. The substrates used were pre-cleaned micro slides purchased from Gold Seal Products, and <100> orientation, 2-inch diameter silicon wafers purchased from International Wafer Service. Before depositing the films, substrates were base cleaned for 15 min at 70°C on a hot plate in a mixture of 50 mL of 30% NH<sub>4</sub>OH, 50 mL of 30% H<sub>2</sub>O<sub>2</sub>, and 250 mL of deionized (DI) water. After rinsing with DI water, the substrates were then acid cleaned for 15 min at 70°C on a hot

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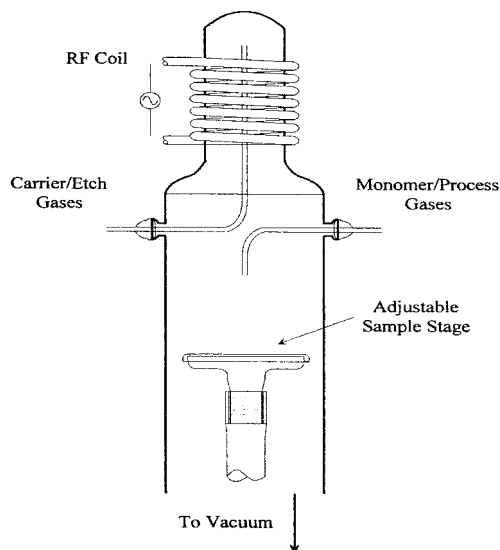


Figure 1 RF Plasma polymerization reactor.

plate in a mixture of 50 mL of HCl, 50 mL of 30%  $\text{H}_2\text{O}_2$ , and 250 mL of DI water. The cleaned substrates were next rinsed with DI water and then were kept in the vacuum oven for 10 min at 120°C for drying.

### Plasma-polymerized films

Plasma-polymerized films were produced in a glass tubular reactor using a 13.56 MHz generator (RF plasma products), the power being inductively coupled through external electrodes (see Figure 1). The electric field, when applied to the gaseous monomers at low pressures (0.1–1.0 Torr), produces active species that may react to form highly cross-linked polymer films. In these experiments, argon was used as the primary plasma, and the monomer vapor was injected downstream of the primary argon glow discharge, as shown in Figure 1.

For these experiments, the adjustable sample holder was kept farthest away from the glow discharge to get uniform films. Because of the distance from the monomer inlet to the substrate, a high RF power was used (300 W) to prepare plasma-polymerized benzene films. The pressure inside the reactor chamber was 700 mTorr. The argon flow rate was kept constant at 40 SCCM for all films of benzene. In contrast, the benzene flow rate was varied from 5 to 10 SCCM to get benzene films of different thickness. The conditions used to prepare plasma-polymerized furan films were 300 W RF power, 500 mTorr system pressure, 15 SCCM argon flow rate, and 5–10 SCCM furan flow rate (the flow rate was varied to get films with different thickness). All films for materials characterization were prepared for a 30-min deposition time.

## Film characterization and measurements

### Ellipsometer

A variable angle spectroscopic ellipsometer (WVASE32, J. A. Woollam Company, Inc.) was used to measure the thickness of the plasma-polymerized thin film. All studies were performed on films prepared on silicon wafers.

### FTIR spectroscopy

FTIR was used to analyze the chemical structure of the plasma-polymerized thin films. FTIR spectra of the monomer liquids and plasma-polymerized thin films were recorded with a BIO-RAD FTS 40 spectrometer in the 4000–400  $\text{cm}^{-1}$  range. A drop of each of the respective liquid monomers was placed between two thin KBr pellets to record the IR spectrum of the monomers. Plasma-polymerized films of benzene and furan prepared on Si wafers were used for the FTIR analysis.

### XPS

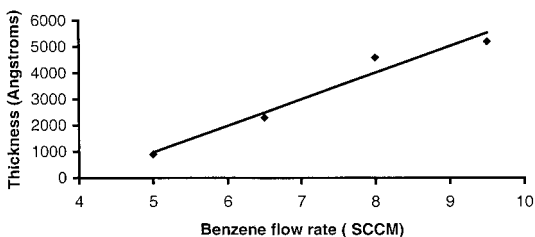
Plasma-polymerized films of benzene and furan prepared on Si wafers were used for the XPS analysis. Small samples were examined in a Surface Science Instruments' M-Probe spectrometer. This instrument was equipped with a monochromatic Al X-ray source for photoelectron production. Samples were mounted on an aluminum holder with care to ensure that the surfaces to be examined were not touched in any manner, and then transferred through air into the spectrometer via a load-lock. The pressure in the chamber during analysis was between 2 and 4  $\times 10^{-8}$  Torr. The overall surface composition was monitored by taking survey scans from 0 to 1000 eV binding energy. The analysis area on the sample was  $\sim 400 \times 1000 \mu\text{m}$ , with the depth analysis of the order of 10 nm.

### UV-vis absorption spectroscopy

UV-vis absorption spectroscopy was used to determine the presence and extent of conjugation in the plasma polymerized thin films.<sup>10</sup> UV-vis absorption spectra of the monomer liquids and plasma polymerized thin films were recorded with a U-3000 Hitachi Spectrophotometer. Plasma-polymerized thin films on microslides with blank microslides as reference were used for UV-vis spectra.

### PL spectroscopy

PL spectroscopy was performed at room temperature with UV excitation at 365 nm from a filtered Hg



**Figure 2** Thickness versus flow rate for benzene film deposition.

source. The plasma-polymerized thin films deposited on Si wafers were used for the PL analysis.

## RESULTS AND DISCUSSION

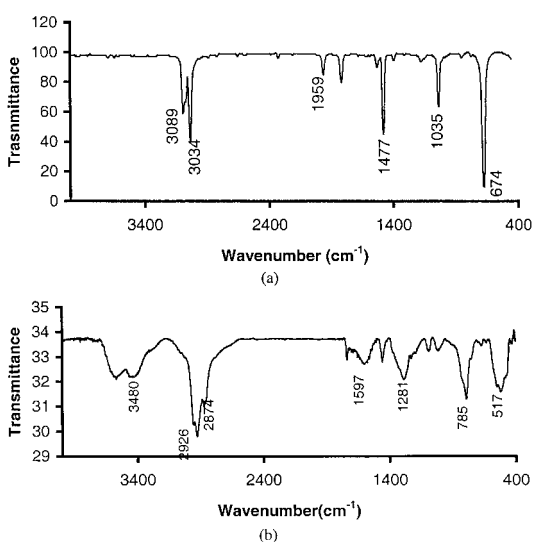
### Plasma-polymerized thin films of benzene

#### Ellipsometry

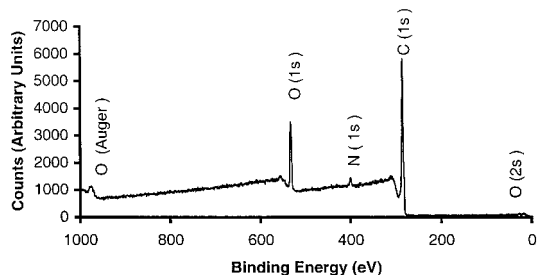
The thickness versus benzene flow rate data obtained while keeping the RF power and argon flow rate constant are shown in Figure 2. The thickness of the films increased linearly with the increase in benzene flow rate over the range studied.

#### FTIR spectroscopy

The FTIR spectra of the benzene monomer and plasma-polymerized benzene thin film are shown in Figures 3a and 3b, respectively. Both spectra show notable differences in the peaks. The pure benzene monomer spectrum has characteristic peaks at 3089 and 3034  $\text{cm}^{-1}$  for the aromatic CH stretch. It also has peaks at 1527 and 1477  $\text{cm}^{-1}$  for the presence of the benzene ring.



**Figure 3** (a) IR spectra of benzene monomer. (b) IR spectra of plasma-polymerized benzene film.



**Figure 4** XPS survey spectrum of a plasma polymerized benzene film.

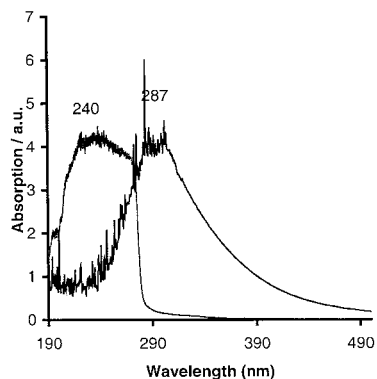
The FTIR spectrum of the plasma-polymerized benzene thin film shows peaks at 2930 and 2866  $\text{cm}^{-1}$  for aliphatic  $\text{CH}_2$  and  $\text{CH}_3$  stretching modes, respectively. It also shows a peak at 1460  $\text{cm}^{-1}$  for  $\text{CH}_2$  bending. This result indicates the opening of the aromatic ring present in the original benzene monomer. The spectrum also has a peak at 1600  $\text{cm}^{-1}$ , which shows the presence of the aromatic ring in the structure of the plasma-polymerized film. Furthermore, the peak at 787  $\text{cm}^{-1}$  indicates the presence of 1 : 2 : 3-substituted and 1 : 3-substituted benzene rings. Finally, the spectrum has a peak at 3480  $\text{cm}^{-1}$ , which indicates the presence of bonded OH in the film. Therefore, by comparing both the IR spectra, we can conclude that we have successfully formed a very highly cross-linked plasma-polymerized thin film of benzene with some degree of aromatic ring opening.

#### XPS

The atomic composition of the plasma-polymerized benzene films was analyzed by XPS. As shown in Figure 4, three bands appear in the XPS spectra of plasma-polymerized benzene films: a carbon band around 284.6 eV, a nitrogen band around 399.5 eV, and an oxygen band around 532.4 eV. Hence, as observed in the FTIR spectra, the presence of oxygen in these films is obvious. This oxygen may be due to the atmospheric oxygen present in the reactor. The atomic concentration for benzene films determined from the band area and calibration factors are listed in following Table I.

**TABLE I**  
Characteristics of Plasma-Polymerized Benzene Films

Element	Binding Energy (eV)	Area (a.u.)	Sensibility Factor	Concentration (%)
C1s	284.6	48306	1.00	83.39
O1s	532.4	19823	2.49	13.73
N1s	399.5	2802	1.68	2.88



**Figure 5** UV-Vis absorption spectra for benzene monomer and plasma polymerized benzene film.

#### UV-vis absorption spectroscopy

The UV-vis absorption spectra of the pure monomer and plasma-polymerized thin film of benzene are shown in Figure 5. The pure benzene shows a peak at 240 nm, which can be attributed to the  $\pi \rightarrow \pi^*$  transition of the aromatic benzene ring. From the spectrum of the plasma-polymerized benzene film, it can be seen that there is a red shift of  $\sim 47$  nm in  $\lambda_{\text{max}}$  compared with the monomer peak. It is well known that increasing the extent of conjugation generally moves the absorption to longer wavelengths.<sup>10</sup> So, this red shift in plasma-polymerized benzene indicates the presence of an increased degree of conjugation present in the film formed.

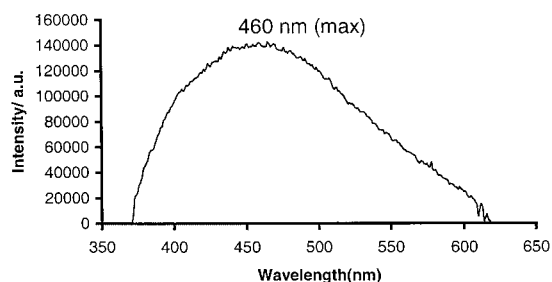
#### PL spectroscopy

The PL spectrum of the plasma-polymerized thin film of benzene is shown in Figure 6. It can be seen from the spectrum that these films show a blue emission with a broad peak showing a maximum at  $\sim 460$  nm.

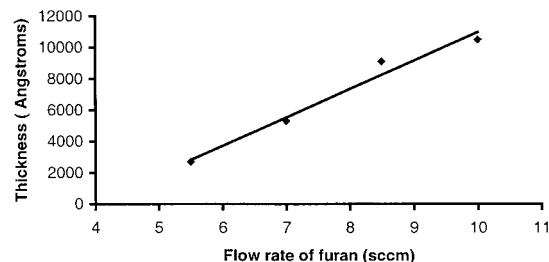
#### Plasma-polymerized thin films of furan

##### Ellipsometry

The thickness versus furan flow rate data obtained while keeping the RF power and argon flow rate con-



**Figure 6** PL spectrum for plasma polymerized benzene film.



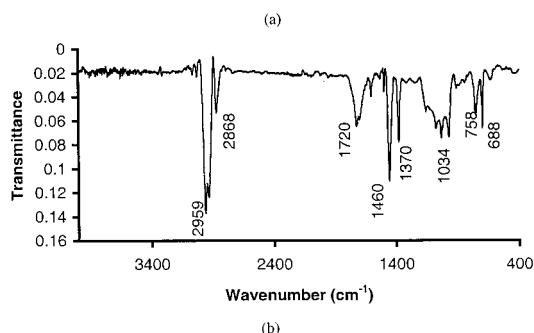
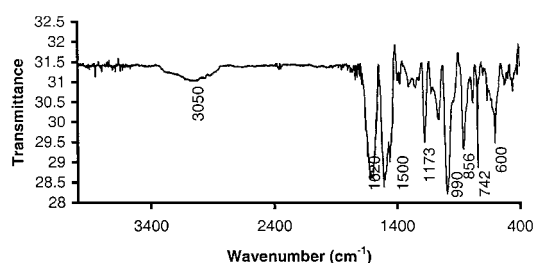
**Figure 7** Thickness versus flow rate for furan film deposition.

stant are shown in Figure 7. The thickness of the films increased linearly with the increase in furan flow rate over the range studied.

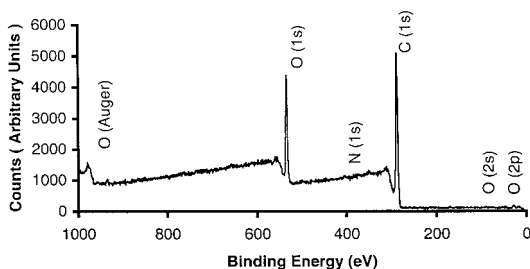
#### FTIR spectroscopy

The FTIR spectrum of the furan monomer and plasma-polymerized furan thin films are shown in Figures 8a and 8b, respectively. Both spectra show wide differences in the peaks. The pure furan monomer shows characteristic peaks at  $3050\text{ cm}^{-1}$  for the aromatic CH stretch. It also shows a peak at  $1620\text{ cm}^{-1}$ , which represents the furan ring. There is a peak at  $742\text{ cm}^{-1}$  that can be attributed to furan ring vibrations.

The FTIR of a plasma-polymerized furan thin film shows peaks at  $2960$  and  $2868\text{ cm}^{-1}$  for aliphatic  $\text{CH}_2$  and  $\text{CH}_3$  stretch. It also shows a peak at  $1458\text{ cm}^{-1}$  for  $\text{CH}_2$  bending. This result indicates the opening of the aromatic ring of the original furan monomer. The spectrum it also shows a peak at  $1720\text{ cm}^{-1}$ , which indicates the presence of cyclopentanone in the struc-



**Figure 8** (a) IR spectra of furan monomer. (b) IR spectra of plasma polymerized furan film.



**Figure 9** XPS survey spectrum of plasma polymerized furan film.

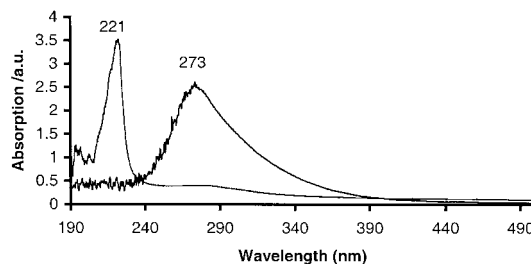
ture of the plasma-polymerized film. Finally, the peak at  $755\text{ cm}^{-1}$  that is present in the original monomer is reduced in intensity, indicating the cross-linking of the furan monomer and the formation of 2:5-substituted furan ring. So, by comparing both the FTIR spectra, we can conclude that we have successfully formed very highly cross-linked plasma-polymerized thin films of furan.

#### XPS

The atomic composition of the plasma-polymerized furan films was analyzed by XPS. As shown in Figure 9, three bands appear in the XPS spectra of plasma-polymerized benzene films: a carbon band around 284.6 eV, a nitrogen band around 398.9 eV, and an oxygen band around 532.3 eV. Hence, the presence of a small amount of nitrogen in these films is obvious. This nitrogen may be due to the atmospheric nitrogen present in the reactor. The atomic concentration for benzene films determined from the band area and calibration factors are listed in Table II.

#### UV-vis absorption spectroscopy

The UV-vis absorption spectra of the pure monomer and the plasma-polymerized thin film of furan are shown in Figure 10. The furan monomer shows a maximum absorption ( $\lambda_{\text{max}}$ ) at 221 nm, which can be attributed to the  $\pi \rightarrow \pi^*$  transition of the aromatic ring. From the spectra of plasma-polymerized furan film it can be seen that there is a red shift of  $\sim 52\text{ nm}$  in  $\lambda_{\text{max}}$  compared with the monomer peak. It is well known that increasing conjugation generally moves



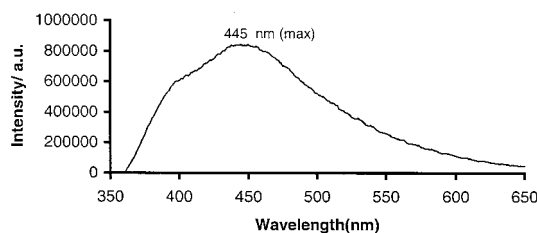
**Figure 10** UV-Vis absorption spectra for furan monomer and plasma polymerized furan film.

the absorption to longer wavelengths.<sup>10</sup> This red shift in plasma-polymerized furan demonstrates an increased degree of conjugation present in the resulting films.

#### PL spectroscopy

The PL spectrum of the plasma-polymerized thin film of furan is shown in Figure 11. For the preparation of efficient LEDs, it is important to have materials with a range of emission wavelengths that exhibit high emission quantum efficiency.<sup>11</sup> It can be seen from the spectrum that the plasma-polymerized furan films prepared here show a blue emission with a broad peak with maximum at  $\sim 445\text{ nm}$ .

From the results obtained here for the plasma-polymerized thin films of benzene and furan, it can be concluded that plasma polymerization is a good technique for fabricating uniform and reproducible thin films of desired thickness of these organic materials. This technique gives highly cross-linked polymerized thin films with an increased amount of conjugation present in the films produced. The films thus produced were also found to show blue emission, as seen in the PL spectra of the films. It is believed that the same excited states give rise to both PL and EL emission,<sup>12</sup> so it can be assumed that if these materials show efficient EL spectra, then it will also be in blue region as that of PL spectra. Further work is in progress to fabricate these films in actual devices and obtain EL from these materials in multilayered device structures.



**Figure 11** PL spectrum for furan film.

**TABLE II**  
Characteristics of Plasma-Polymerized Furan Films

Element	Binding Energy (eV)	Area (a.u.)	Sensitivity Factor	Concentration (%)
C1s	284.6	44086	1.00	79.54
O1s	532.3	27839	2.49	20.15
N1s	398.9	287	1.68	0.31

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