

## RAMAN SPECTROSCOPY AND PHOTOLUMINESCENCE CHARACTERIZATION OF THE IODINE DOPED PLASMA- POLYMERIZED BIPHENYL THIN FILM

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**ABSTRACT.** The iodine doped plasma-polymerized biphenyl thin film is investigated in this study. Iodine atoms lead to increase the charge transfer complexes and change the electronic equilibrium in the polymer structure due to their high electronegativity. Therefore, the iodine doped films show significant improvements in the electrical characteristics as compared to the undoped ones. The results of Raman spectroscopy verify the presence of the iodined groups in the structure of deposited thin films. The number density of the iodined groups increases with increasing the radio frequency input power. The ID/IG ratio changes in a range from 0.40 to 0.72 for the undoped thin films while it decreases from 0.74 to 0.58 for the iodine doped thin films which can be due to the rearrangement in the structure. Photoluminescence spectra show a broad red emission band at about 630 nm as well as unclear bands placed like small shoulders at 580 nm and 731 nm. These bands become to seem clearly after the iodine doping process. The conjugation length of the polymer thin films increases with iodine doping as well as increasing the power values. All depositions are produced using a capacitively coupled plasma system with 13.56 MHz radio frequency source. During the doping process, the vaporized iodine material is directly exposed to the plasma discharge and mixed with the biphenyl polymer material. All results are characterized in detail.

### 1. INTRODUCTION

The plasma discharge is most commonly used to produce polymer thin films, namely plasma polymerization [1], [2]. It is a type of dry processing method and provides an opportunity to work at room temperature, no solvent requirements, and the ability to coat an arbitrarily shaped object [2], [3]. Different than conventional chemical deposition methods, pin-hole free polymer thin films are produced with high crosslinking and branching structures [1], [4]. Moreover, plasma polymerized thin films have higher quality and homogeneity and provide good adhesion due to increasing the degree of bondability as compared to conventional methods [1].

Plasma polymerization is mostly used for  $\pi$ -conjugated organic materials among the polymer materials due to their excellent electronic properties and good chemical stability [5]–[7]. These properties make them very favorable for several applications such as photovoltaics, light emitting diodes, optical coatings, and biomedical areas [4], [8]–[13]. Biphenyl ( $C_{12}H_{10}$ ), a type of  $\pi$ -conjugated organic material, is an aromatic hydrocarbon including two benzene rings connected with a C-C bond. Due to its easy processing structure, the molecule of biphenyl is used as a source of the aromatic ring [3]. It can efficiently react with other molecular structures and provide an opportunity to form new compounds with easy control.

The doping process is a commonly used technique to increase the electronegativity of the polymer thin film and improve its electrical properties [9]. Iodine ( $I_2$ ), which has a high electronegativity, is one of the most used dopant materials [14]–[18]. It is a very compatible dopant material to act other materials. Iodine doping leads to change the electronic equilibrium of polymer molecule and increases the concentration of the charge transfer complexes in the structure. Therefore, iodine atoms perform as electron acceptors and improve the electrical conductivity of the polymer.

In this study, the plasma-polymerized biphenyl ( $C_{12}H_{10}$ ) thin films are produced using a capacitively coupled radio frequency (RF) plasma system. The iodine dopant material is used to improve their electrical characteristics. The deposition and doping process of thin films are carried out at variable RF input power values (100 W, 200 W, and 300 W), the deposition time (20 min), and the pressure (0.2 Torr). The undoped and the iodine doped plasma-polymerized biphenyl thin films are investigated using the measurements of Raman spectroscopy and Photoluminescence. The results of the characterization are discussed in detail in Section 3.

## 2. EXPERIMENTAL SET UP

The experimental set up consists of a vacuum chamber including two parallel cylindrical electrodes, as shown in Figure 1. 13.56 MHz RF power supply is used, and the RF power is applied between the electrodes to generate the plasma discharge. Thin films are produced on glass samples. Biphenyl material is purchased from Sigma-Aldrich Company, ReagentPlus<sup>®</sup>, 99.5%. Solid biphenyl, melting at 69 °C, is evaporated into a reservoir by heating up to 130 °C. The volatile biphenyl is introduced into the vacuum chamber where the backfill pressure is about  $10^{-3}$  Torr. As the biphenyl vapors fill the chamber, a pressure of 0.2 Torr, the RF power is activated. Iodine doping material is purchased from Sigma Aldrich Company, ACS reagent,  $\geq 99.8\%$ . During the doping process, the iodine is placed into a heating

reservoir at 200 °C and then introduced into the chamber directly by mixing with the biphenyl vapors.

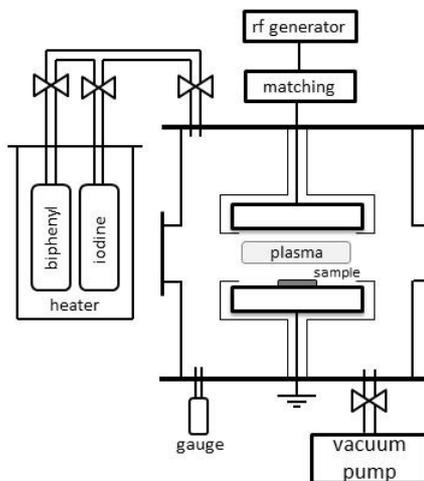


FIGURE 1. Scheme of capacitively coupled RF plasma system

### 3. CHARACTERIZATION

#### 3.1. Raman Spectroscopy

The chemical structures of the deposited thin films are investigated using Raman spectroscopy. The data are collected in a range from 150  $\text{cm}^{-1}$  to 1850  $\text{cm}^{-1}$  with a scan step of 2.2  $\text{cm}^{-1}$ . The Raman spectroscopy is performed using a Horiba-Jobin Yvon i550 system which includes a CCD camera and an Nd:YAG laser with a 532 nm wavelength.

The Raman spectra of the undoped thin films are shown in Figure 2 for 100 W, 200 W, and 300 W of RF input power. Peak intensities of the spectra show a decrease with increasing the power values. This is due to variable rearrangements occurring at different power values. During the plasma deposition, the first breaking is expected for the C-C bond between benzene rings of the biphenyl molecule. Then, H atoms dissociate from the benzene rings, and they fragment to smaller compounds. As a result, various fragments and compounds such as alkane, alkene and alkynes groups can be generated. These fragments react with other activated species. When unsaturated fragments/structures interact with each other, new saturated compounds

with more heavy masses are generated. During this time, the observed reactions are significantly dependent on the energy of the plasma discharge.

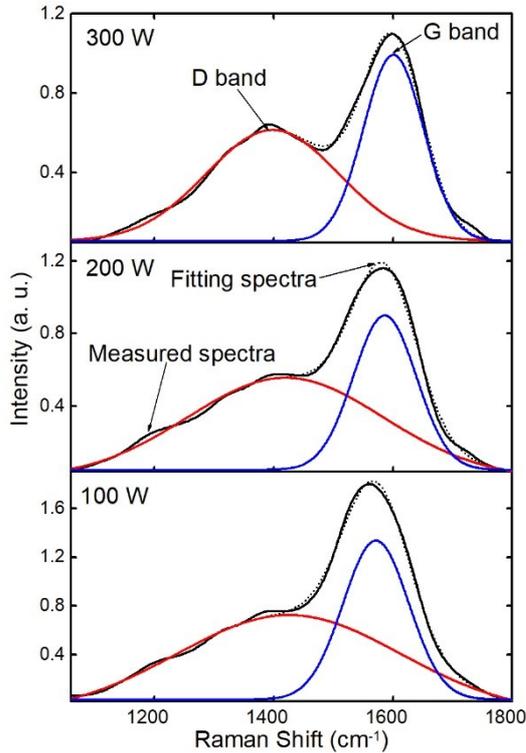


FIGURE 2. The D and G bands of the undoped thin films

The Gaussian fitting method is applied to the spectra, and the D and G bands are investigated. While the D band shifts from  $1425\text{ cm}^{-1}$  to  $1419\text{ cm}^{-1}$  and  $1408\text{ cm}^{-1}$ , the G band shifts from  $1571\text{ cm}^{-1}$  to  $1586\text{ cm}^{-1}$  and  $1594\text{ cm}^{-1}$  with increasing the RF input power. The intensities ratio of the D and G bands ( $I_D/I_G$ ) is calculated, and an increase from 0.40 to 0.72 is obtained by increasing the power. According to Dwivedi et al. [19], the  $I_D/I_G$  ratio can be correlated with the  $sp^3/sp^2$  ratio. Therefore, it can be considered that the thin films generated at the higher power have relatively higher  $sp^3$  content. Moreover, the formation of  $\pi$ -type bonds is obtained with good quality due to the transfer of the high energy to the film structure.

The Raman spectra of the iodine doped thin films are shown in Figure 3. Iodine material has a high electronegativity and behaves more activated as exposed to the plasma discharge. The formed iodine radicals react with the fragments of the biphenyl molecules and generate new iodined compounds. The spectra show a

strong band at  $179\text{ cm}^{-1}$  referring to the  $\text{I}_5^-$  ion group [20]. A weak and broad band observed at  $241\text{ cm}^{-1}$  corresponds to the existence of molecular iodine ( $\text{I}_2^0$ ) [21], [22]. These seen bands verify the presence of the iodined groups in the structure of the deposited films. The iodine content increases with increasing the power. This shows the higher energy of the plasma discharge leads to more interactions and combinations with iodine atoms. In addition to the expected reactions, some side-reactions are also observed due to the iodine [14]. According to these side-reactions, hydrogen atoms removed from benzene rings connect with iodine atoms to generate HI molecules. These HI molecules react with CH groups. Then, fragments of the biphenyl molecule react with other iodine radicals, and this leads to form the mono-substitutions of aromatic structures.

As compared to the results of the undoped ones, the G band of the iodine doped films is achieved at higher wavenumbers, shifting from  $1583\text{ cm}^{-1}$  to  $1592\text{ cm}^{-1}$  and  $1600\text{ cm}^{-1}$ . The D band is obtained at lower wavenumbers, shifting from  $1417\text{ cm}^{-1}$  to  $1401\text{ cm}^{-1}$  and  $1385\text{ cm}^{-1}$ . This shifting in the wavenumber can be related to the rearrangement of the length of the  $\pi$ -delocalized structures [23]. The  $I_D/I_G$  ratio decreases from 0.74 to 0.58.

Additionally, a broad band near  $1160\text{ cm}^{-1}$ , especially observed at 300 W, occurs due to the C-C stretching vibrations [22]. The spectra show the intensities of the D and G bands decrease after the iodine doping. It can be due to the structural modifications resulting from the interactions between the iodine and the biphenyl polymer lattice [22].

### 3.2. Photoluminescence

Photoluminescence (PL) spectra are acquired for the undoped and the iodine doped plasma-polymerized biphenyl thin films. PL spectra are collected using a Newport MS257TM monochromator equipped with Hamamatsu C7041 detector head. A 532 nm laser is used as an excitation source for room temperature. PL spectra of the undoped film show a broad band centered at around 630 nm of the wavelength which is assigned to red emission, as shown in Figure 4. The wavelength of the maximum PL peak exhibits small blue-shifting with increasing the RF input power, which may be due to the recombination of the donor-acceptor pair. The spectra also present two unclear bands giving small shoulders at 580 nm (green emission) and 731 nm (red emission). All locations of the band peaks are found by using a Gaussian decomposition process. This shows that the plasma-polymerized biphenyl thin films have different transitions of energy levels depending on the rearrangement of the structures.

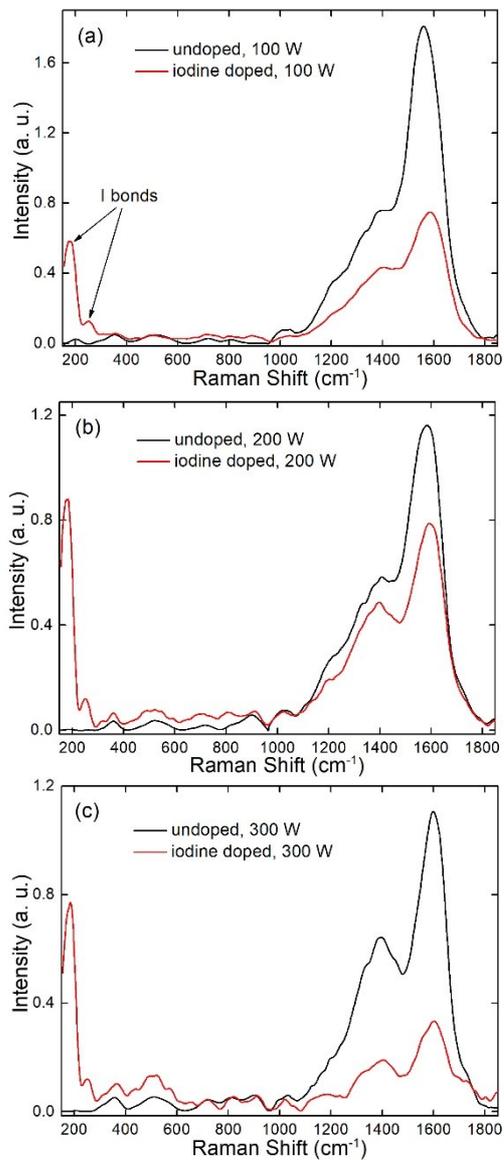


FIGURE 3. The Raman spectra of the undoped and the iodine doped thin films for (a) 100 W, (b) 200 W, and (c) 300 W

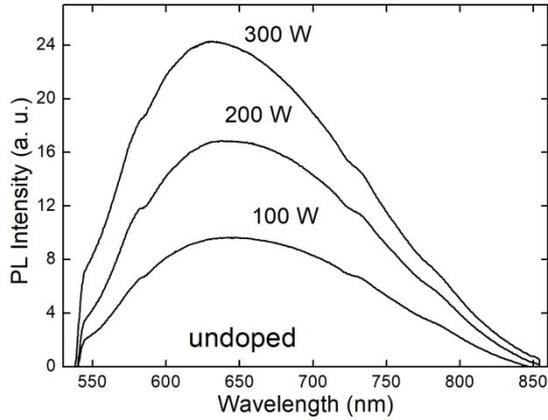


FIGURE 4. PL spectra of the undoped thin films

Figure 4 shows that the intensity of the peaks increases with increasing the RF input power. As seen in Raman spectra, the plasma-polymerized biphenyl thin films have different chemical structures at various power values. Differences in structures lead to change the orientation of the film, which affects the optical characteristics of the polymer. As the number density of the oriented components in the structure increases, the transitions between the ground and the excited states become shorter. Thus emission with high intensity is obtained in the PL spectra [24]. The results show the higher number density of oriented components is observed at higher RF power values.

PL spectra of the iodine doped are shown in Figure 5. PL peak locations are found by using the Gaussian decomposition, and they place at around 580 nm and 630 nm. After the iodine doping, these peaks start to appear clearly. It can be considered that incorporation of the iodine carriers changes the transition process dependent on the levels of bonding. The intensities of the iodine doped spectra decrease as compared to the undoped ones. As iodine atoms react with the biphenyl molecules, they perform as electron-accepting components in the structures. Presence of the iodined groups leads to an increase in the number density of the charge transfer complexes and improves the electrical conductivity of the plasma-polymerized thin film. Additionally, iodine doping rises the conjugation length in the polymer and causes structural modifications. It can be concluded that changes in the structural formation and the increase in the conjugation cause the decrease observed in the intensities of PL peaks [25].

By increasing the RF power, PL intensities also decrease due to the rise in the concentration of the iodined groups in the polymer structure. These groups presenting in the polymer structure utilize the electron transfer as a result of interacting with  $\pi$ -electrons of the aromatic rings. Thus, the charge transfer is provided from the lowest unoccupied molecular orbital (LUMO) level of the iodine doped groups to the conduction band of polymer [26].

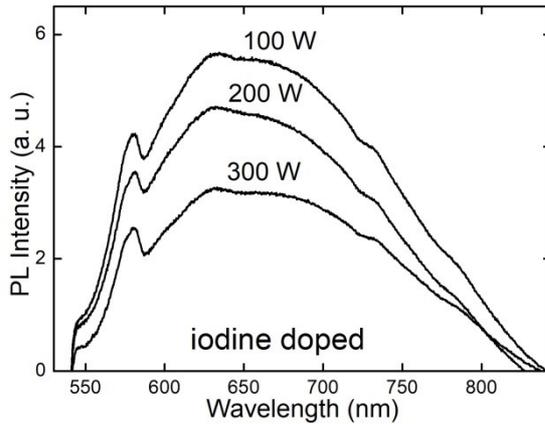


FIGURE 5. PL spectra of the iodine doped thin films

#### 4. CONCLUSION

The undoped and the iodine doped plasma-polymerized thin films are studied using a capacitively coupled RF plasma discharge. RF plasma discharge causes structural changes at different power values dependent on the rearrangement. These changes lead to a decrease in the intensities of Raman spectra as the RF power increases. Additionally, the  $I_D/I_G$  ratio changes from 0.40 to 0.72. The Raman spectra of the iodine doped thin films prove the existence of the iodined components in the structure and their concentration increases at higher power values. Iodine atoms lead to more interactions occurring with the biphenyl compounds at the higher power values. The  $I_D/I_G$  ratio of the doped films decreases from 0.74 to 0.58. PL spectra exhibit the deposited films have different transitions of energy levels in their structures. After the doping process, the PL intensities decrease with increasing the power values. This shows the extension is observed in the conjugation length of the structure.

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