

Effect of iodine doping on the bandgap of plasma polymerized aniline thin films

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Abstract

Pure and iodine-doped polyaniline thin films are prepared by ac plasma polymerization technique. Doping of iodine is carried out *in situ* as well as by employing iodine chamber methods. The structural analyses of pure and iodine-doped polyaniline thin films are carried out by FTIR spectroscopic studies. Optical bandgaps of these films are evaluated from UV–VIS absorption studies. Direct and indirect transition energy gaps are determined from Tauc plots. The structural changes of polyaniline upon doping and the reduction of optical bandgap are explained on the basis of the results obtained from FTIR spectroscopic and UV–VIS absorption studies.

1. Introduction

The employment of plasma polymerization for synthesis of novel thin film materials has become attractive and has been an active area of research in the recent past [1]. Originally this technique was employed to coat passive layers, but the current trend is to extend this technology to other applications as well, in which device performances are influenced by surface compositions. Controllability and reproducibility of the surface composition of plasma polymerized thin films is of utmost important to achieve superlative performance. It is known that several reaction parameters like power input, monomer flow rate, monomer vapour pressures, substrate temperature and positioning of substrates relative to the plasma zone influence the structure and composition of plasma polymerized thin films [2–6]. The advantage of employing ac plasma polymerization technique is that it permits the synthesis of high-quality polymer films at low power inputs [7]. It is now recognized that under low power input conditions, the functional groups of the starting monomer are retained in the plasma polymerized films [8, 9]. By employing ac plasma polymerization technique it is possible to synthesize polymers having linear rather than crosslinked structures [10].

The investigations of the optical properties of polymer thin films have gained attention due to their potential applications

in optical sensors, LEDs and as antireflective coatings [11, 12]. The effect of doping on the bandgap of polyaniline is already dealt with [10, 13], but a systematic study on the stability and the structure of the *in situ* iodine doped plasma polymerized aniline films has not been reported. Here, we report the preparation and optical properties of plasma polymerized aniline thin films. *In situ* iodine doping is carried out to investigate the effects of doping on the optical bandgap. UV–VIS studies are carried out to determine the optical bandgap and other optical parameters of plasma polymerized aniline thin films. FTIR studies are carried out to elucidate the structure of plasma polymerized aniline thin films and also to investigate the effect of doping on the structure of the plasma polymerized aniline thin film.

2. Experimental

Ac plasma polymerization technique is employed for the deposition of polyaniline thin films. Details of the experimental set-up are given elsewhere [7]. In brief, it consists of two circular electrodes of diameter 0.23 m each and 2×10^{-3} m thick, placed in parallel at a separation of 0.05 m. Ultrasonically cleaned glass substrates are placed on the lower stainless steel electrode for polymer thin film deposition. The glow discharge chamber is evacuated and a discharge is obtained between the electrodes by applying a low

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frequency (50 Hz), high ac voltage (500–800 V) and controlled by a current in the range of 40–70 mA. Then the monomer aniline is injected into the plasma zone by means of a sprayer at a monomer vapour pressure of 0.2 Torr. Polymer thin films are deposited under optimum conditions on the substrates, which are kept on the lower electrode.

2.1. Iodine doping

Two different types of iodine doping are attempted. In the first case iodine chamber method is used and in the second case *in situ* iodine doping is employed. The details of the techniques adopted are discussed below.

2.1.1. Iodine chamber method. In this method, iodine crystals are placed in a glass beaker and the films to be doped are kept above this glass beaker. As the beaker is slowly heated, the iodine vapours are absorbed into the polymer films kept above the glass beaker. The time of doping is 15 min. Due to doping, the colour of the polyaniline thin film changes from light to dark brown.

2.1.2. *In situ* iodine doping. For *in situ* iodine doping, an additional iodine sprayer is incorporated in the plasma deposition chamber. Both monomer and the dopant iodine are sprayed simultaneously into the plasma zone, so that the polymer films deposited on the glass substrates have iodine incorporated in the structure.

2.2. Characterizing techniques employed

These films are then subjected to different characterization techniques like FTIR spectroscopy and UV–VIS absorption studies for elucidating the chemical structure and estimating the bandgap of the polyaniline, respectively. Polyaniline is scraped from the glass substrates and is mixed with KBr before pelletizing. These pellets are then loaded into the sample holder compartment of Nicolet Avatar 360 FTIR spectrophotometer to record the spectra. UV–VIS spectra of pure and iodine-doped polyaniline and heat-treated polyaniline thin film samples are recorded using Hitachi U3410 UV–VIS–NIR spectrophotometer.

3. Results and discussion

3.1. FTIR analysis

3.1.1. Undoped polyaniline. The FTIR spectra of monomer aniline and plasma polymerized aniline are shown in figure 1. The band assignments of the FTIR absorption peaks for pure polyaniline are given in table 1. The polyaniline spectrum corresponding to the pure sample shows peaks at 1600, 1500 and 1450 cm^{-1} indicating that the aromatic ring is retained in the polymer [14]. The peak at 3020 cm^{-1} is due to C–H stretch and N–H vibration is observed at 3370 cm^{-1} . Primary aromatic amine C–N stretch is observed at 1310 and 1250 cm^{-1} . Substituted benzene peaks are also detected at 750 and 694 cm^{-1} . These indicate that most of the infrared absorption features characteristic of the monomer aniline are retained in the plasma polymerized aniline samples. It can be seen that the peaks become broader, which is typical of a highly disordered nature of plasma polymers.

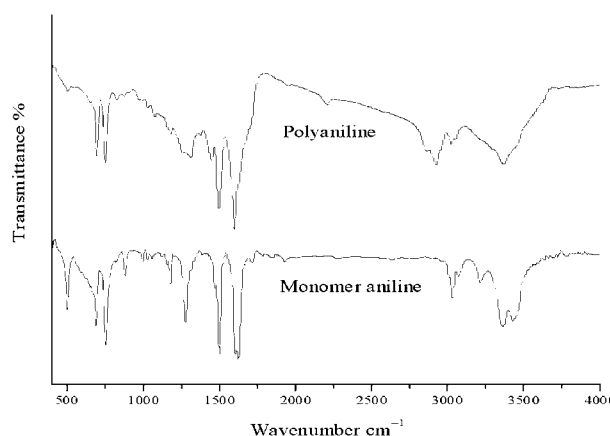
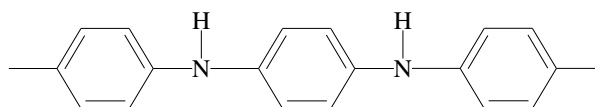


Figure 1. FTIR spectra of monomer aniline and plasma polymerized aniline.

Table 1. Assignments of FTIR absorption band of undoped and iodine-doped polyaniline.

Polyaniline (wavenumber cm^{-1})	Assignment	Iodine doped polyaniline (wavenumber cm^{-1})
3370	N–H	3350
3020	C–H stretch	3030
2920	C–H stretch	2920
1600	Ring stretch	1590
1500	Ring stretch, C–H bending	1496
1450	Ring stretch	1446
1310	C–N stretch	1300
1250	C–N bending	1250
752	C–H out of plane deformation	752
694	C–H out of plane deformation	694

The FTIR spectrum of both monomer and plasma polymerized aniline are compared for their respective functional groups. From the foregone discussions it has been established that the aromatic ring is retained in the polymer and the possible mechanism of polymerization of aniline is because of hydrogen abstraction; a tentative structure is shown below.



3.1.2. *In situ* iodine-doped polyaniline. The FTIR spectra of pure and iodine-doped polyaniline is shown in figure 2. The assignments of the FTIR absorption bands for pure and iodine-doped polyaniline are also given in table 1. It is clear from table 1 that in the iodine-doped polyaniline there is a shift in N–H stretching and C–N stretching bands. The N–H stretch shifts towards lower wavenumber, 3350 cm^{-1} . The C–N stretch at 1310 cm^{-1} , for the pure polyaniline, shifts towards 1300 cm^{-1} in the iodine doped sample. The shifts observed in N–H and C–N stretching bands indicate that the iodine atoms might be getting attached to the amine nitrogen sites of polyaniline [14]. The key bands corresponding to the aromatic rings in the iodine-doped polyaniline are found to be shifted to lower frequencies, 1590, 1496 and 1446 cm^{-1} .

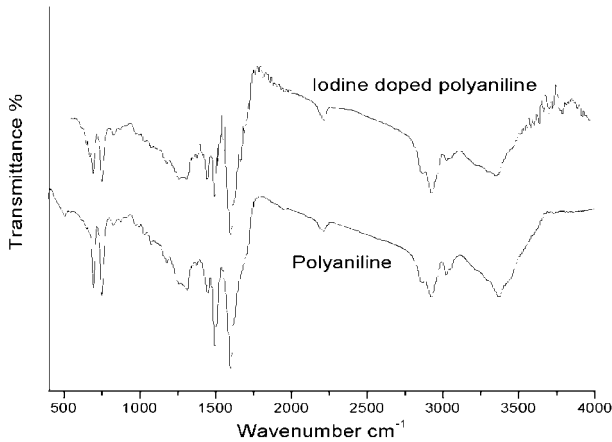


Figure 2. FTIR spectra of polyaniline and *in situ* ion doped polyaniline.

This is an indication that iodine doping is effecting a change in structure of plasma polymerized aniline samples.

3.2. UV-VIS absorption studies

3.2.1. *Iodine chamber method.* Iodine chamber method doped polyaniline thin films are subjected to UV-VIS absorption studies. From the spectrum, αd (product of absorption coefficient and thickness) values are available directly. Hence the absorption coefficient can be evaluated, if the thickness of the sample is known. The thickness of the polymer films is measured by a home made device based on interferometric techniques (Tolansky) and the thickness values lie in the range of 1200–2000 Å.

The absorption coefficient (α) is plotted against the photon energy ($h\nu$) for pure and iodine-doped polyaniline thin films and is shown in figure 3. The intercept of this plot on the photon energy axis gives the bandgap (E_g) of the polyaniline. It is evident from the figure 3 that there is a considerable reduction in the bandgap for iodine-doped polyaniline sample. The bandgap of pure polyaniline sample is found to be 3.04 eV and that of doped polyaniline film is 1.8 eV.

Iodine-doped polyaniline is heat-treated at 100°C for 5 h in an oven to test the stability of these films. The absorption spectra of these heat-treated films are then recorded and the bandgap is evaluated. It is found that the bandgap of heat-treated polyaniline drastically increased to 3.01 eV, which is almost the same as that of undoped polyaniline thin film, as shown in figure 4.

The observed increase in the bandgap upon heating of the doped sample is due to the escape of iodine, which is likely to have got adsorbed and bonded loosely to the surface of the film. The observed facts indicate that this method of iodine doping is not effective in incorporating iodine into the polymer chain. Hence *in situ* method of iodine doping is carried out so as to effect a permanent change in the bandgap of plasma polymerized aniline thin films.

3.2.2. *In situ iodine doping.* *In situ* iodine doping is carried out as described in section 2.1.2. The absorption spectra of these *in situ* doped thin film samples are then recorded. From figure 5 it is observed that in the low energy region the edges

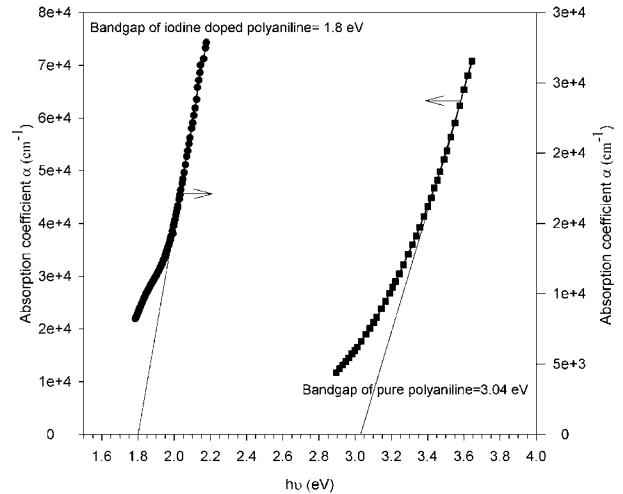


Figure 3. Bandgap of pure and iodine-doped polyaniline thin film doped by iodine chamber method.

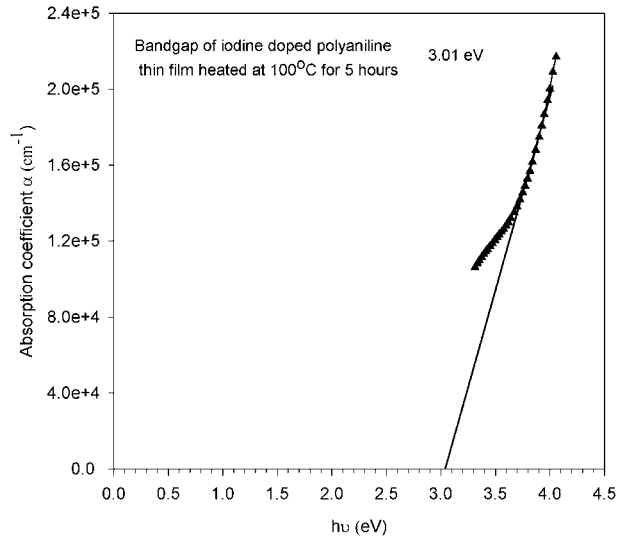


Figure 4. Bandgap of heat-treated polyaniline doped by iodine chamber method.

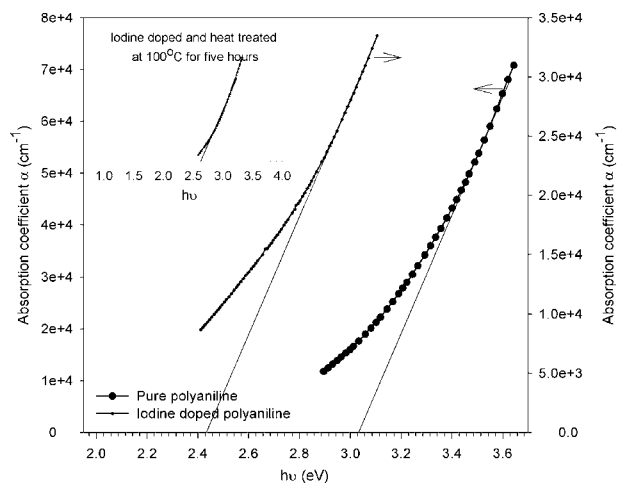


Figure 5. Bandgap of pure polyaniline, *in situ* iodine-doped polyaniline and heat-treated polyaniline thin films.

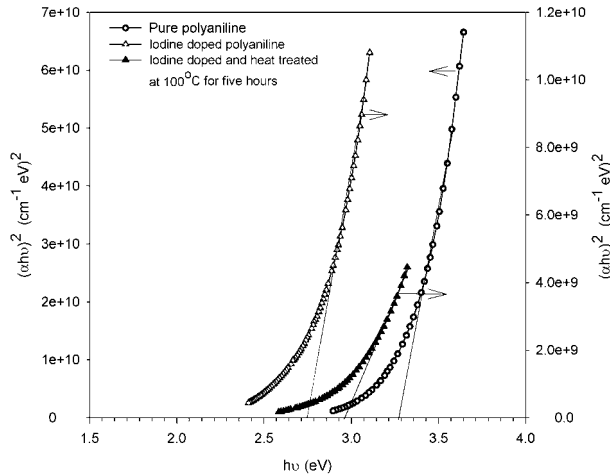


Figure 6. Direct allowed transition energies of pure, *in situ* iodine doped, and heat-treated polyaniline thin film.

follow an exponential fall in these plasma polymerized aniline samples. The appearance of this exponential tail is due to lack of absence of long-range order in these samples [15]. It may be pointed out that there is already complimentary evidence to this effect from the FTIR spectrum. Further, these curves are characterized by two slopes indicating the presence of both direct and indirect transitions in the pure, iodine doped and heat-treated polyaniline thin films. The photon absorption in many amorphous materials is found to obey the Tauc relation [16], which is of the form

$$\alpha hv = B(hv - E_{\text{opt}})^n$$

Here α is the absorption coefficient, $h\nu$ the photon energy, B a constant and the index n is connected with the distribution of the density of states. The index $n = \frac{1}{2}$ corresponds to the direct allowed transition energy gap and $n = 2$ represents the indirect allowed transition energy gap [17].

To determine the direct and indirect transition energy gaps, plots of $(\alpha hv)^2$ as a function of photon energy ($h\nu$), and $(\alpha hv)^{1/2}$ vs $h\nu$ are plotted and are shown in figures 6 and 7, respectively. The intercept of these curves on the photon energy axis gives the direct and indirect transition energy gaps [18, 19]. The bandgap (E_g) values along with the direct (E_d) and indirect (E_{id}) transition energies for the pure, iodine doped and heat-treated samples are listed in table 2.

The optical bandgap of pure polyaniline is found to be 3.04 eV, whereas iodine doped samples exhibit a low bandgap of 2.42 eV as shown in figure 5. The reduction in the bandgap due to iodine doping may be due to the incorporation of iodine into the polymer chain and, thereby, extending the density of states more into the visible region of the electromagnetic spectrum as compared to that of the undoped case (iodine has a broad absorption band extending from the UV well into the visible region of the electromagnetic spectrum).

To test the stability of the iodine doped films, these films are heat-treated at 100°C for 5 h in an oven and then the absorption spectrum is recorded. It is found that there is an increase in the bandgap (2.61 eV) of the heat-treated polyaniline thin film as shown in figure 5. This increase in

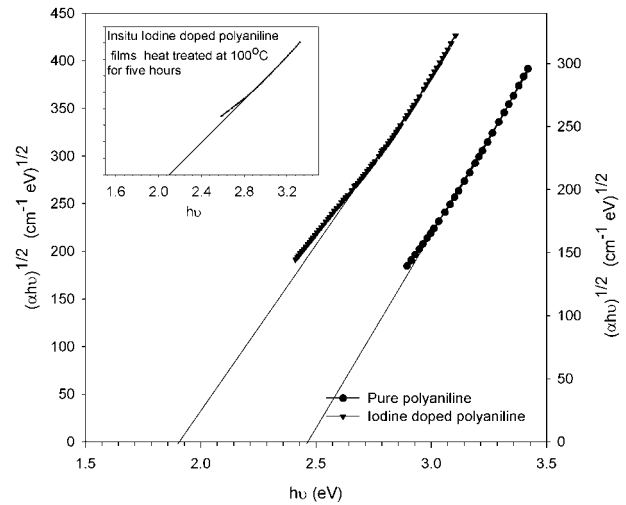


Figure 7. Indirect allowed transition energies of pure, *in situ* iodine doped, and heat-treated polyaniline thin film.

Table 2. Bandgap and direct allowed and indirect allowed transition energy gap of plasma polymerized aniline thin films.

Sample name	Bandgap (eV)	Direct allowed transition energy gap (eV)	Indirect allowed transition energy gap (eV)
Polyaniline undoped	3.04	3.34	2.44
Iodine doped polyaniline	2.42	2.75	1.91
Doped polyaniline heated at 100°C for 5 h	2.61	2.94	2.12

the bandgap may be due to the removal of iodine atoms that are adsorbed on the surface or loosely bonded to the polymer.

Subsequent heat treatment of these samples does not produce any change in the bandgap, suggesting that the reduction in the bandgap upon iodine doping is permanent and stable. FTIR spectroscopic studies revealed that there is a change in the structure of iodine-doped polyaniline samples. These observations clearly indicate that *in situ* iodine doping reduces the bandgap considerably and the film is found to be stable up to a temperature of 100°C. The change in bandgap could be due to structural changes introduced by doping.

4. Conclusions

Polyaniline thin films are prepared by ac plasma polymerization technique. Iodine doping is carried out by the iodine chamber method and also by *in situ* doping. FTIR spectroscopic studies reveal that the aromatic ring and the infrared absorption features characteristic of the monomer aniline are retained in the plasma polymerized aniline sample. The most probable mechanism of polymerization of aniline is due to hydrogen abstraction. The bandgap of the iodine chamber doped sample has shown a drastic reduction. However, upon heat treatment, it is observed that the bandgap has increased almost to the undoped value. In the *in situ* doped polyaniline thin films, the bandgap first reduces and heat treatment only slightly increases the bandgap. Subsequent heating does not

change the bandgap. Hence, *in situ* method of doping is more reliable and the change effected in the bandgap is permanent.

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