

Research Article

Effect of Iodine Doping on the Characteristics of Polyaniline Thin Films prepared by Aerosol Assisted Plasma Jet Polymerization at Atmospheric Pressure

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Accepted 05 Sept 2014, Available online 01 Oct 2014, Vol.4, No.5 (Oct 2014)

Abstract

Iodine-doped polyaniline thin films are prepared by aerosol assisted plasma jet polymerization at atmospheric pressure and room temperature. The doping of iodine was carried out in situ by employing iodine crystals in aniline monomer by weight mixing ratios of 1%, 3%, 5% and 7%. The chemical composition analyses of pure and iodine-doped polyaniline thin films are carried out by FTIR spectroscopic studies. The optical band gaps of the films are evaluated from absorption spectrum studies. Direct transition energy gaps are determined from Tauc plots. The structural changes of polyaniline upon doping and the reduction of optical band gap are explained on the basis of the results obtained from FTIR spectroscopy, UV–VIS absorption studies, X-ray diffraction and atomic force microscope (AFM) analysis. The energy band gap will be different according to the concentration of polyaniline iodine. It can be concluded that it can be prepared Iodine-doped polyaniline thin films by aerosol assisted plasma jet polymerization and control the optical energy band gap regularly by controlling the aniline -iodine weight mixing ratios.

Keywords: Polyaniline iodine doping, thin films, optical properties, band gap, XRD.

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 (Biederman H and Slav Ynska D, 2000). 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 most important to achieve superlative performance. It is known that several reaction parameters like power input, monomer flow rate, monomer vapor pressures, substrate temperature and positioning of substrates relative to the plasma zone influence the structure and composition of plasma polymerized thin films (Shi F. F., 1996; Agostino R. D., 1990). 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 (Nagagawa K., 1990; Koike Y, *et al*, 1990). The effect of doping on the band gap of polyaniline is already dealt with (Chaudhar H. K. and Kelkar D. S., 1997; Tauc J., 1970) 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, a report the preparation and optical properties of plasma polymerized aniline thin films. In situ iodine doping is carried out by aerosol assisted plasma jet polymerization at atmospheric pressure and room temperature to investigate the effects of doping on the optical band gap. UV–VIS studies are carried out to determine the optical band gap and other optical parameters of plasma polymerized aniline thin films. FTIR studies are carried out to elucidate the effect of doping on the chemical structure of the plasma polymerized aniline thin films (Davis E. A. and Mott N. F., 1970).

Experimental

Iodine-doped polyaniline thin films have been prepared by aerosol assisted plasma polymerization. Thin films were prepared by dielectric barrier discharge plasma jet a homemade (Hammad R. Humud, *et al*, 2014). The thin films were deposited on glass substrates. Pure aniline monomer was used as the organic precursor. Figure (1) schematic diagram for the non-equilibrium atmospheric pressure plasma Iodine-doped polyaniline thin films preparation. Argon gas with flow rate of 1 L/min passes through the nobilizer which contains a mixture of iodine and aniline with weight mixing ratios of 1%, 3%, 5% and 7%. the mixture convert to aerosol, this aerosol was guided by the Ar gas to the plasma jet. the plasma was ignited by using an electric source at a fixed frequency of 28.0 kHz. The plasma was generated downstream to the substrate which was positioned suatabal distance from the

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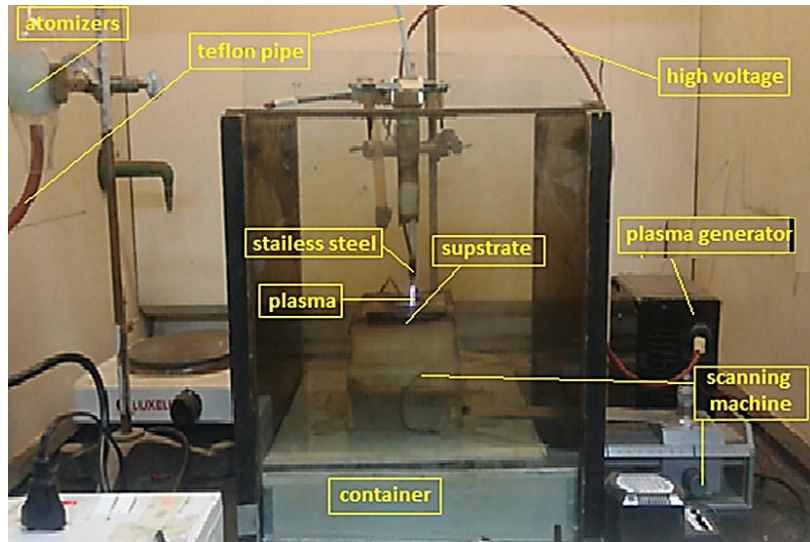
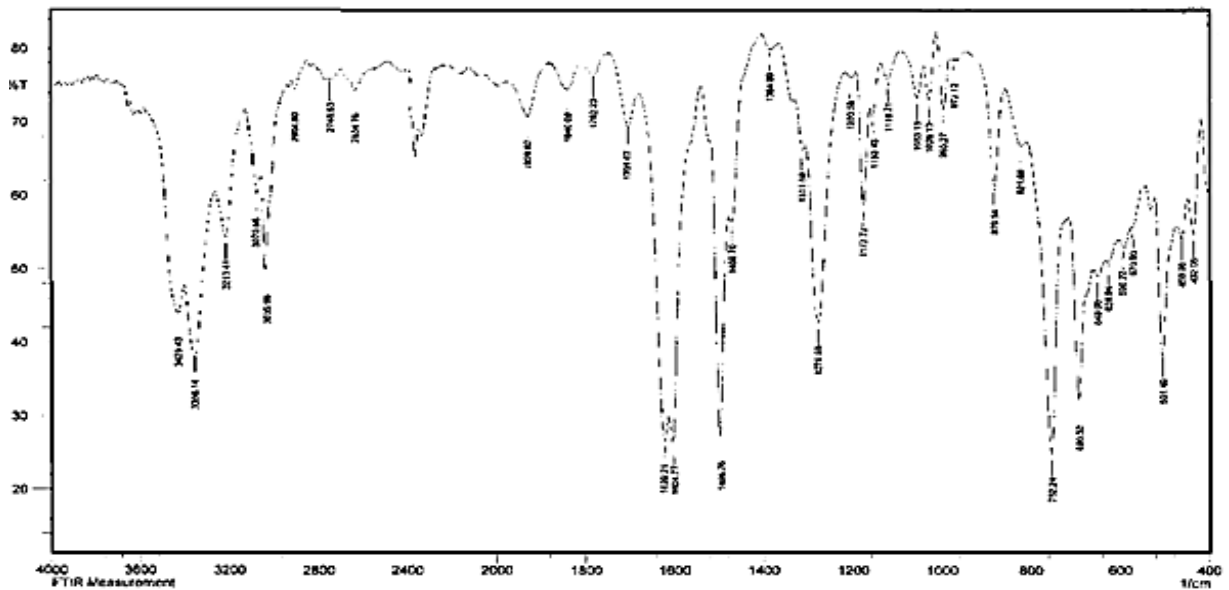
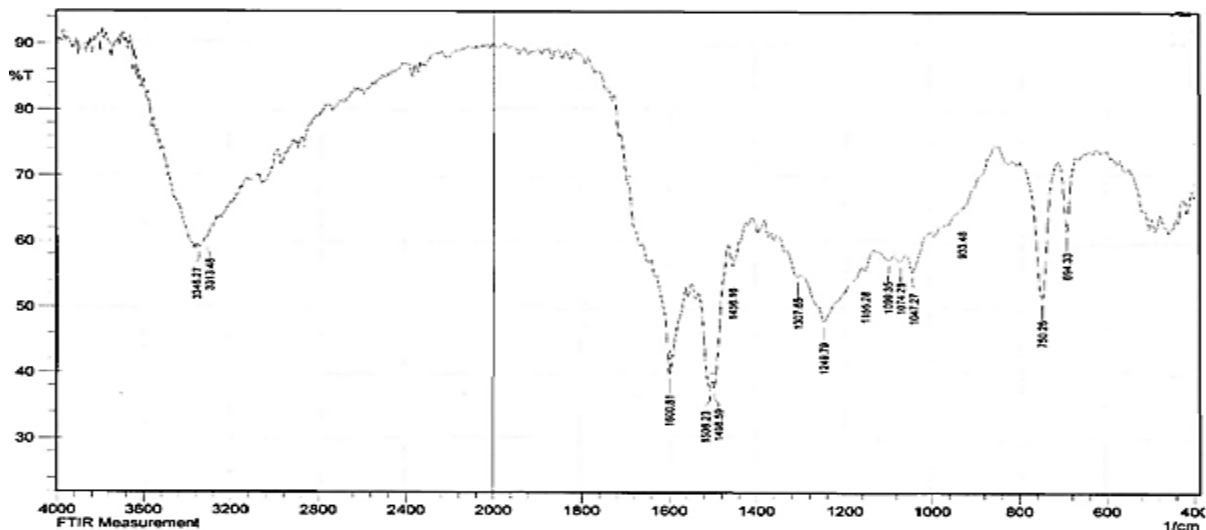


Figure 1: Schematic diagram for the non-equilibrium atmospheric pressure plasma Iodine-doped polyaniline thin films preparation experimental set-up



a



b

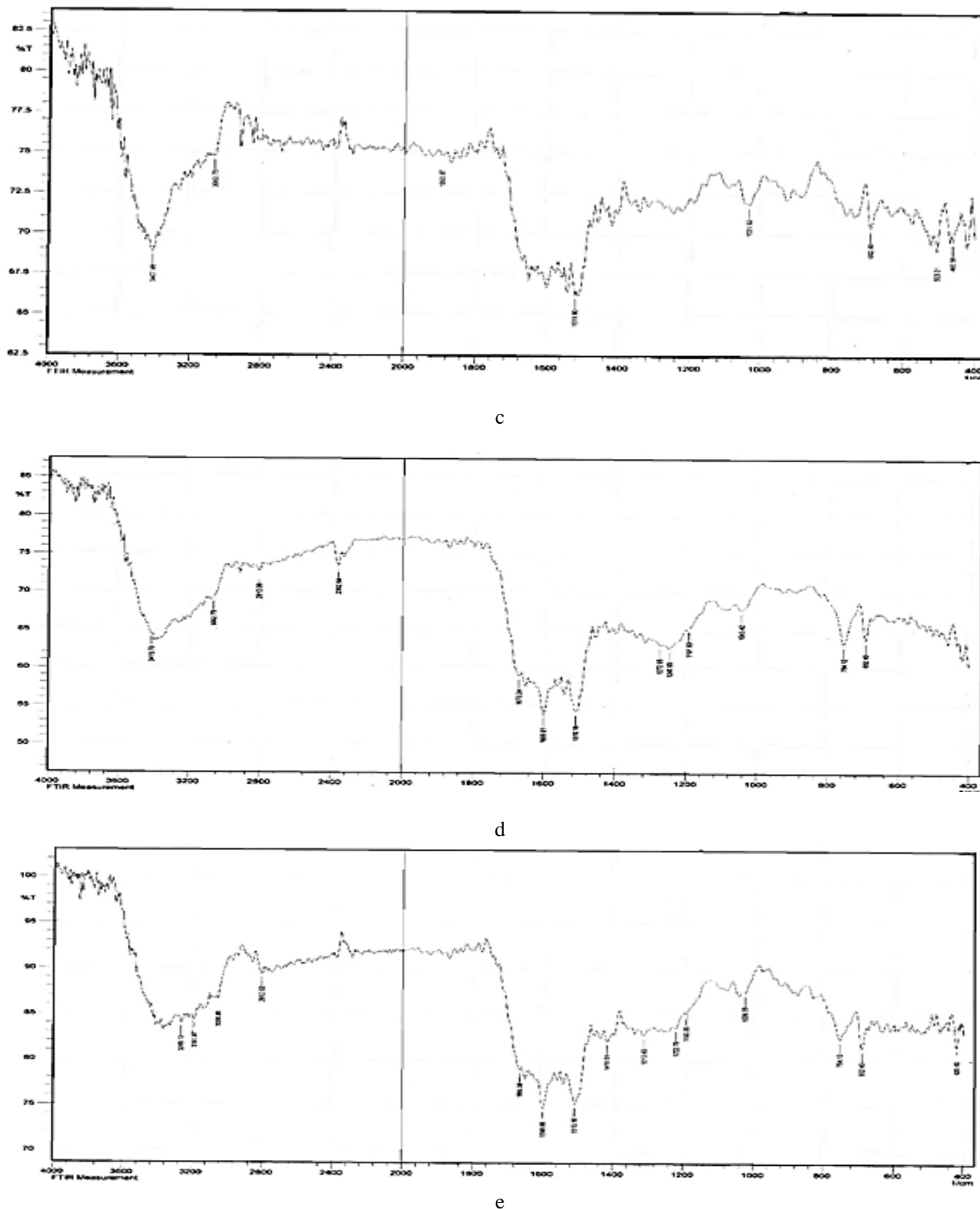


Figure 2: FTIR spectra a for aniline monomer, b for polyaniline thin films without doping c for 3% iodine doping d for 5% iodine doping and e for 7% iodine doping polyaniline thin films .

plasma torch end. The film deposition was carried out for 5 min under constant carrier gas flow rate and the substrate at room temperature. The substrate moved on the x and y direction mechanically for the purpose of obtaining a homogeneous films thickness a long the substrate area.

The Film thickness was measured using the optical interferometer method A double –beam UV-VIS-NIR

210A Spectrophotometer was used to measure the absorption Iodine-doped polyaniline thin films which deposited at different iodine concentration in the range of (200-1200) nm. The background correction was taken for each scan. The absorption data with films thickness can be used to calculate absorption coefficients of the films at different Wave length, which have been used to determine the energy band gap E_g .

Table 1: Assignments of FTIR the absorption bands for pure monomer, polyaniline, and iodine-doped polyaniline

Assignment	Mono-aniline (wavenumber cm ⁻¹)	polyaniline (wavenumber cm ⁻¹)	Iodine- doped polyaniline (wavenumber cm ⁻¹)- 3%	Iodine- doped polyaniline (wavenumber cm ⁻¹)- 5%	Iodine- doped polyaniline (wavenumber cm ⁻¹)-7%
N-H	3356	3356	3407	3415	3296
C-H stretch	3035	3033	3062	3062	3055
C-H stretch	2904	2956	-----	2810	2812
Ring stretch	1620	1604	1893	1610	1598
Ring stretch	-----	1512	-----	-----	1419
C-H bending	-----	-----	-----	-----	-----
Ring stretch	1469	1456	1519	1510	1313
C-N stretch	1311	1334	-----	1245	1222
C-N bending	1276	1250	1013	1143	-----
C-H out of plane deformation	752	757	692	754	754
C-H out of plane deformation	690	673	505	692	692

FT-IR spectra were recorded by using solid KBr discs and testing all samples by Shimadzu Co. FT-IR 8000 series Fourier transform, infrared spectrophotometer from wavelength range 400–4000 cm⁻¹ under identical conditions. The morphological surface analysis is carried out employing an atomic force microscope (AA3000 Scanning Probe Microscope SPM, tip NSC35/AIBS) from Angstrom Ad-Vance Inc. In order to study the structural properties, the structure is analyzed with a SHIMADZU 6000 X-ray diffractometer system which records the intensity as a function of Bragg's angle. The source of radiation is Cu- α with wavelength $\lambda = 1.5406 \text{ \AA}$, current 30mA and voltage 40 kV. The scanning angle 2θ is varied in the range of 10 – 80 degree with aspeed of 5 deg/min.

Results and discussion

A. FTIR analysis

The FTIR spectra of aniline as a monomer and Iodine-doped polyaniline thin films polymerized by plasma shown in Figure (2).

The polyaniline spectrum, Figure (2-b) shows peaks at 1620, 1500 and 1450 cm⁻¹ indicating that the aromatic ring is retained in the polymer (Hammad R. Humud, *et al*, 2014). The peak at 3035 cm⁻¹ is due to C–H stretch, also the N–H vibration is observed at 3356 cm⁻¹. Primary aromatic amine C–N stretch is observed at 1311 and 1276 cm⁻¹. Substituted benzene peaks are also detected at 752 and 694 cm⁻¹. The FTIR spectrum for both monomer and plasma polymerized aniline are comparable 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.

The band assignments of the FTIR absorption bands for pure, polymerized and iodine-doped polyaniline thin films are given in table 1. It is clear from the table that there is a shift in N–H stretching and C–N stretching bands in the iodine-doped polyaniline. The N–H stretch shifts towards high wavenumber. The shifts observed in N–H and C–N stretching bands indicate that the iodine

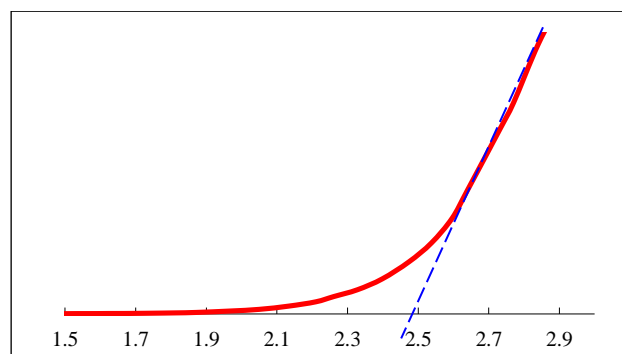
atoms might be getting attached to the amine nitrogen sites of polyaniline (Pankove J. I., 1971). The key bands corresponding to the aromatic rings in the iodine-doped polyaniline are found to be shifted towards high wavenumber. This is an indication that iodine doping causes a change in the structure of the plasma polymerized aniline samples.

B. UV-VIS absorption studies

The photon absorption in many amorphous materials is found to obey the Tauc relation (Pankove J. I., 1971):

$$\alpha h\nu = B(h\nu - E_{opt})^n$$

where (α) is the absorption coefficient, ($h\nu$) is the photon energy, (B) a constant and the index (n) is connected with the distribution of the density of states. The index $n = 1/2$ corresponds to the direct allowed transition energy gap and $n = 2$ represents the indirect allowed transition energy gap (Shah Jalal A. B. M, *et al*, 1996). Figure (4) shows $(\alpha h\nu)^2$ vs. photon energy graph of plasma polymerised aniline in its pure and iodine doped form. It is seen from this figure and table (2) that the iodine doping decreases the optical band gaps from 2.5 eV for pure polyaniline to 2.15 eV for polyaniline doped with 7% iodine. The reduction in the optical band gap is probably due to the modification of the polymer structure. Doping induces a structural ordering of the polymers due to the insert of the charged species. There are signatures supporting these changes in the FTIR and UV- Vis spectra.



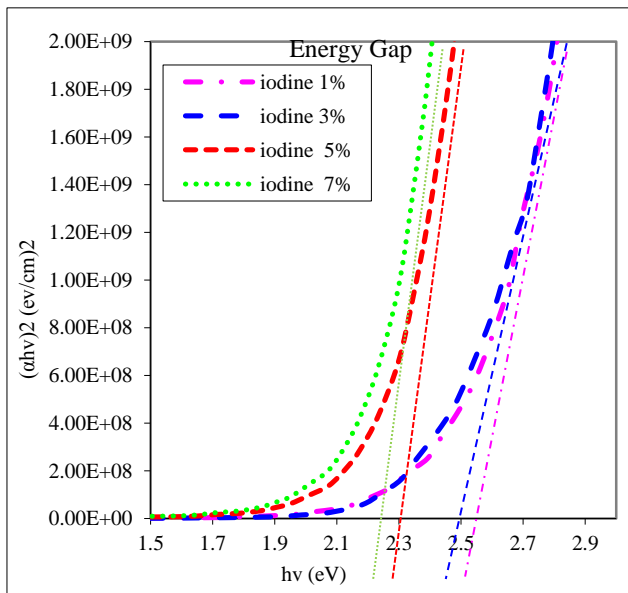


Figure 3: $(\alpha h\nu)^2$ vs. photon energy graph of plasma polymerized aniline thin films a) pure b) iodine doped

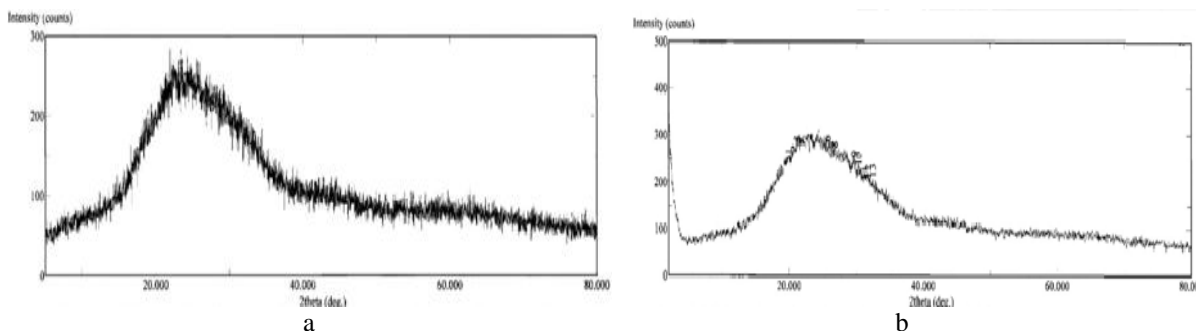


Figure 4: XRD a) for pure polyaniline thin films and b) for 7% iodine doped polyaniline thin films

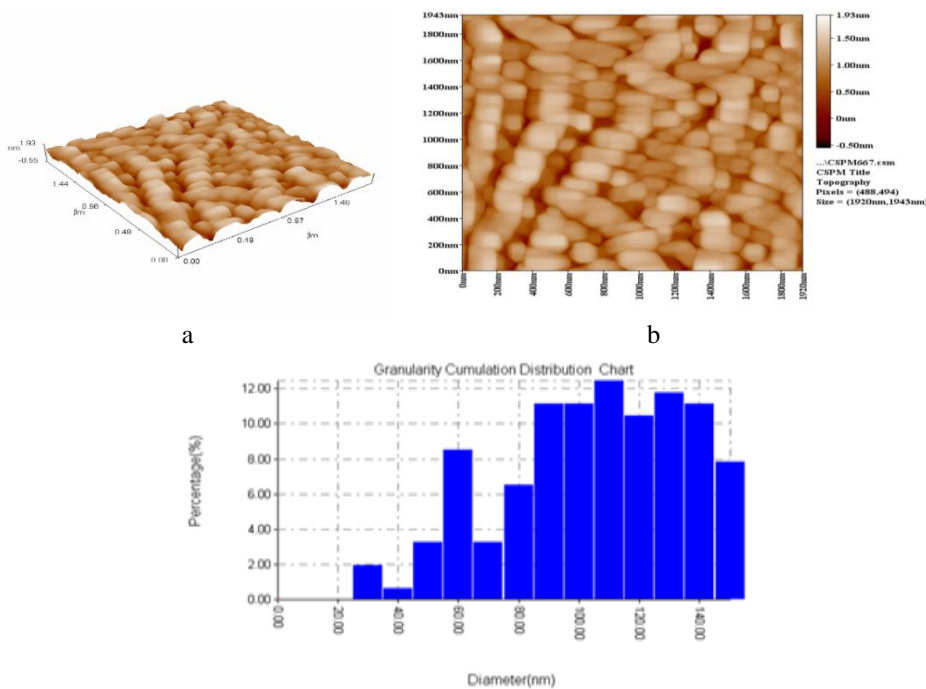


Figure 5: AFM photographs of plasma polymerized pure aniline thin films surface. a) 3D view, b) 2 D view and c) the granulosity distribution chart

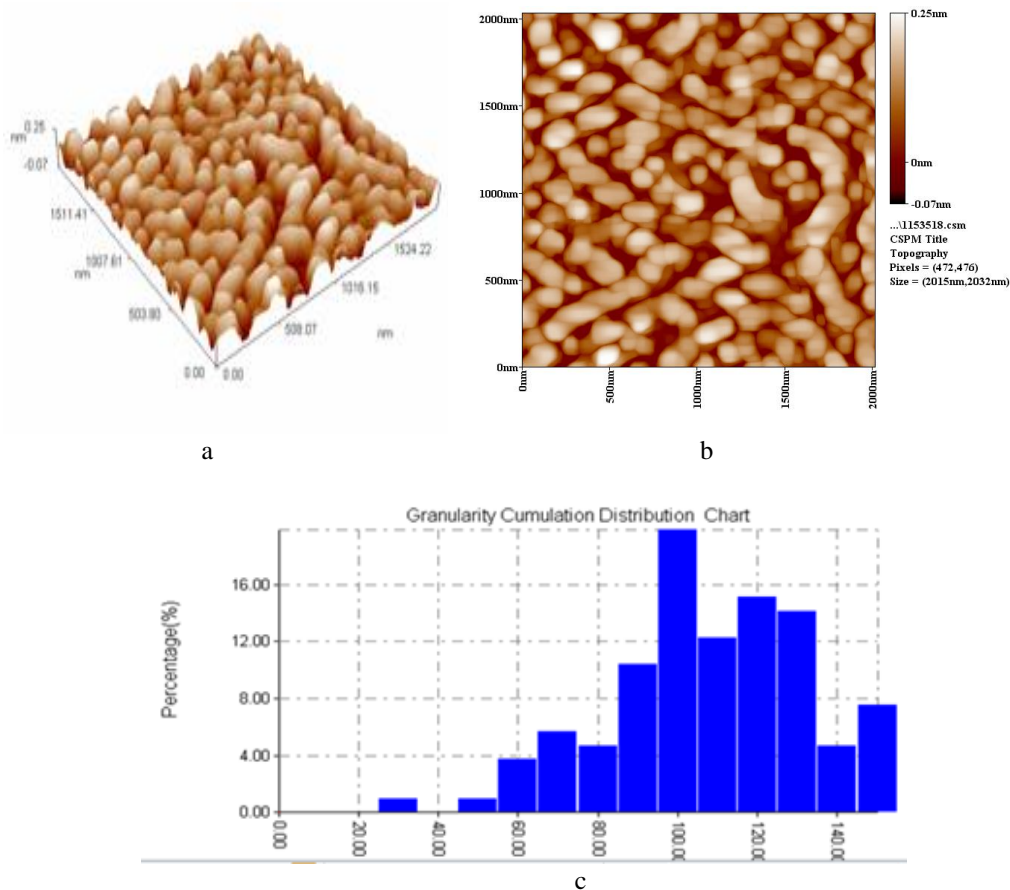


Figure 6: AFM photographs of plasma polymerized 7% iodine doped polyaniline thin films surface. a) 3D view b) 2 D view and c) the granularity distribution chart

Table 2: Energy band gap of plasma polymerized aniline thin films in its pure and iodine doped form

Sample name	Direct allowed transition energy gap (eV)
pure Polyaniline	2.5
1% Iodine doped polyaniline	2.48
3% Iodine doped polyaniline	2.37
5% Iodine doped polyaniline	2.22
7% Iodine doped polyaniline	2.15

C. X-ray diffraction analysis

X-ray diffraction pattern was employed to characterize the structure of the samples. Figure (4-a) shows the pattern of the as-deposited iodine, while Figure (4-b) represents the 7% iodine doped sample. It is clearly indicated that samples are of amorphous structure.

D. Morphology analysis

The surface morphology of pure polyaniline and 7% iodine doped thin films were examined by AFM. The surface roughness of plasma polymerized pure polyaniline thin films 2.2 Å and for the iodine doped thin films 3 Å.

The low surface roughness of plasma polymerized polyaniline confirms that the technique of plasma polymerization can be employed to produce extremely smooth films with very small surface roughness when

compared to films prepared by other techniques. It is clear that the grains are uniformly distributed within the scanning area. Figures (5) represent the 3-D and 2-D photos of the pure polyaniline thin films surface and c shows the granularity distribution chart. The average diameter of clusters is 103 nm. Figures (6) represent the 3-D and 2-D photos of the 7% iodine doped polyaniline thin films surface and c shows the granularity distribution chart. The average diameter of clusters was 100 nm.

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