The Effect of Gamma Irradiation on the Energy Gap of Polyanniline Thin Films Prepared by Non-thermal Plasma Jet

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ABSTRACT

In this paper, we present a new and direct method to prepare nanostructured polyaniline thin films on any surface. This method was developed to improve the mechanical and adherence properties of polyaniline devices used as ionization radiation sensors. Plasma polymerized organic thin films have received a great deal of interest because of their unique characteristics such as: pinhole-free, structurally cross-linked, insoluble and highly adhered. In this work, nanostructures polyaniline (PANI) thin films were prepared by dielectric barrier discharge (DBD) plasma jet polymerization technique. The UV–visible absorption and infrared analysis confirm that a polyaniline is obtained. Optical properties reveal the band gap of the PANI thin film at room temperature is 2.56 eV. Preliminary gamma radiation interaction with the polyaniline shows that the thin film of polyaniline exhibits a linear response that can be used as a dosimeter for the dose range from 0 to 24000 Gy.

Key Word: Polyaniline thin films, Gamma irradiation, Non-thermal plasma jet

Source of Support: Nil, Conflict of Interest: None declared

INTRODUCTION

Polyanilin is one of the most investigated conducting polymers. Due to its high chemical and thermal stability and the ease of polymerization, together with the relative low cost of production it also has the potential of many technological
applications [9]. But the studies of polyaniline subjected to ionizing radiation have not yet attracted application. The present work is a study of the γ-radiation induced changes in physical properties of nanocrystalline polyaniline thin film, deposited onto a glass substrate. Polyaniline film was deposited by plasma polymerization technique includes plasma (state) polymerization which is one of the most powerful methods for surface modification of polymeric materials. Plasma polymerization can be defined as ‘the formation of polymeric materials under the influence of plasma’ [4]. Solid deposits from organic compounds formed in a plasma early as in 1874 [8,1]. Photographic films and thermoluminescent materials are largely used for individual dosimetry of ionization radiation because they present several advantages compared with other devices. However, these passive dosimeters do not provide a direct reading of the dose since they need a further treatment after the irradiation to yield the information about the dose. The present stage of the development of microelectronic technologies makes it possible to design compact, low-power, multifunctional measurement systems with relatively high reliability and immunity to environmental factors [2]. Thus, it has become possible to design a new generation of active dosimeters called electronic personal dosimeters (EPDs). One of the basic problems faced by EPDs designers is the selection of a suitable radiation detector. The development of polymers has contributed to the development of new types of radiation detectors, which can be used for in situ measurements. Among several candidate polymers, polyaniline stands out because its electrical and optical properties can be changed by oxidation of the main chain or protonation of imine nitrogen of the polymer chain. These two doping processes open up a variety of possibilities to design new detector devices. Another positive aspect is the fact that polyaniline is very inexpensive. The effects of gamma radiation on polymers have already been investigated [10,7], and the results indicate linear correlation of polymer conductivity with the applied dose in some cases. The radiation interaction mechanisms with the polyaniline are quite distinct. The radiation interaction is mainly an oxidation process of the main polymer chain yielding a conductivity enhancement for leucoemeraldine and a conductivity decrease for the emeraldine salt, whereas for the second case the ionization radiation induces a doping state in the polymer main chain structure similar to that found in the conventional acid doping process. In this paper we present an alternative method to polymerize aniline by DBD plasma jet polymerization technique. Plasma polymerized organic thin films have received a great deal of interest because of their unique characteristics such as: pinhole-free, structurally cross-linked, insoluble and highly adhered. In this work, nanostructures polyaniline (PANI) thin films were prepared by dielectric barrier discharge plasma jet polymerization technique. This method is different from the conventional method used for polymerization [5]. The optical characterization of the polyaniline was performed at room temperature and the effect of gamma irradiation (60Co) up to a dose of 24kGy was analyzed. It was found that gamma radiation causes significant variations in the aniline optical energy gap and other properties that can be used for the development of real-time radiation sensors.

**Experimental Work**

Pure aniline monomer was obtained from the Chemical Department, College of Science, University of Baghdad and used as the organic precursor. Then non-equilibrium atmospheric pressure plasma is used to polymerization and deposit polyanilines thin films on the cleaned 10×10 mm glass substrate. The schematic diagram thin films deposition by plasma polymerization is shown in Fig.1 plasma jet polymerization technique consists of die
electric barrier discharge with high voltage of sinusoidal shape of 7.5 kV and frequency of 28 kHz peak to peak. Gas mixture consisted of 2 L/min of Ar as the working gas and the monomer gas, which was vaporized by passing the Ar tube through the aniline vessel. This mixture was allowed to flow in through the inlet pipe, and the plasma was ignited by using an electric source at a fixed frequency of 28 kHz. The plasma was generated downstream to the substrate which was positioned along 1 cm distance from the pipe end. Then the polyaniline films irradiated inside 60Co gamma cell (dose rate of 50 Gy/h), the dose range was between 0-24000 Gy.

**Fig. 1**: Schematic diagram for non-equilibrium atmospheric pressure plasma polymerization experimental set-up [9]

**RESULTS AND DISCUSSION**

FTIR spectrophotometer was used to provides information about the chemical bonds by measuring the absorption of PANI films deposited in the range of 400 to 4000cm⁻¹ to ensure that the prepared film was polyaniline. The FT-IR spectra were recorded by using KBr and testing sample by Shimadzu Co. FT-IR 8000 series Fourier transform. Table (1) and Figures (2) shows some vibration bands at 3445, 2981.88, 1492.314, 1292.90, and 1125.68 etc. These values are characteristic of polyaniline chain and are in agreement with theoretical predictions [12].

**Fig. 2**: FTIR spectra for polyaniline thin films prepared by non-thermal low temperature plasma jet at flow 2L /min, 1cm from plasma torch exit and substrate temperature 100°C
Table 1: F T- I R common band and peaks for PANI thin film prepared by plasma polymerization

<table>
<thead>
<tr>
<th>vibration Bond range (cm$^{-1}$)</th>
<th>Observed peaks Position for all Sample (cm$^{-1}$)</th>
<th>Expected vibrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>3100-3500</td>
<td>3464.92</td>
<td>N-H stretching</td>
</tr>
<tr>
<td>3017-2923</td>
<td>2945.1</td>
<td>C-H stretching of aromatic ring</td>
</tr>
<tr>
<td>1600-1500</td>
<td>1598.88, 1508</td>
<td>C=C stretching of quinoid ring(N=Q=N)</td>
</tr>
<tr>
<td>1400-1480</td>
<td>1458</td>
<td>C=C stretching vibration of benzenoid ring(N-B-N)</td>
</tr>
<tr>
<td>1300-1200</td>
<td>1367, 1244</td>
<td>C-N stretching of primary aromatic amines</td>
</tr>
<tr>
<td>1100</td>
<td>1105.14</td>
<td>C-H bending vibration</td>
</tr>
</tbody>
</table>

Fig. 3 shows the X-ray diffraction for PANI thin films prepared by plasma polymerization at room temperature. This figure shows that the polyaniline thin film is an amorphous material [6].

Fig. 4 shows AFM images for the prepared polyaniline thin film from these images can see that the thin films surface is very soft and smooth. Table 2 shows the thin films preparation conditions and its surface properties obtained from the AFM image (average grain size and average roughness (nm)).

Table 2: Preparation conditions and AFM images information PANI thin films deposited by plasma polymerization

<table>
<thead>
<tr>
<th>Gas flow (L/min)</th>
<th>Distance (cm)</th>
<th>Substrate temperature (°C)</th>
<th>Average grain size (nm)</th>
<th>Average roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1</td>
<td>100</td>
<td>117.55</td>
<td>0.135</td>
</tr>
</tbody>
</table>

Fig. 4: AFM surface morphology of PANI thin films deposited by plasma polymerization
THE OPTICAL ENERGY GAP

The optical energy gap values ($E_g$) for PANI thin films have been determined, by plotting $(\alpha h\nu)^2$ versus $h\nu$ with different irradiation dose are shown in Figs. (5a,b,c and d).

![Graphs](image)

**Fig (5a, b, c and d):** Optical energy gap ($E_g$) for polyaniline thin films prepared by non-thermal low temperature plasma jet at different irradiation dose.
Table 3 shows the energy gap for PAIN thin films irradiated by different gamma-ray doses. The values of the optical energy gap decrease with the increasing of irradiation dose as shown in Fig. 6.

<table>
<thead>
<tr>
<th>Eg (eV)</th>
<th>Absorbed Dose (kGy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.57</td>
<td>0</td>
</tr>
<tr>
<td>2.25</td>
<td>1.1</td>
</tr>
<tr>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td>1.88</td>
<td>24</td>
</tr>
</tbody>
</table>

Fig. 6: Energy gap for PIN thin films before and after irradiated with different gamma doses

It is worth to mention that high energy gamma radiation interacts with the matter in three different ways i.e. photoelectric effect, Compton scattering and pair-production, which are responsible for modifications depends upon the energy of gamma ray photons. For Co-60, it is Compton Effect that dominates. It is well known that in the Compton Effect the momentum of the incident photon is shared between inelastically scattered photon and the ejected electron, and not transferred to atom or nuclei, so, gamma ray photon remains with sufficient energy to knock out an atom from its position after gamma irradiation. Micro strain, dislocation density and distortion parameters decrease with an increase in gamma dose. PIN thin film irradiated by gamma ray may be caused to formation new bonds due to the crosslinks of polyaniline chain after irradiation [11]. The present work is attempted to study the effect of gamma radiation on the structural properties of polyaniline thin films. The study of the radiation effects on polymer will be useful for gamma ray dosimeter.

**Conclusions**

From this study, we can conclude that the optical energy gap were systematic decreasing with increasing gamma ray doses, this systematic change in optical energy gap for gamma ray can be used for measuring gamma dose.

**References**