Structural, optical, morphological and electrical characteristics of polyaniline for device applications

I D Sharma**, P K Saini & V K Sharma

*Department of Physics, S S V College, Hapur, Ghaziabad 245 101, India

*Polymeric & Soft Materials Section, CSIR-National Physical Laboratory, New Delhi 110 012, India

Received 6 March 2012; accepted 17 September 2012

Polyaniline has been chemically synthesised by oxidative polymerization of 0.1 M aniline monomer using 0.3 M dodecyl benzene sulphonic acid (DBSA) as a dopant. The formation of polymer has been confirmed by X-ray diffraction and FTIR measurements where as surface morphology has been observed using scanning electron microscope. The spin coated polyaniline film has been prepared over ITO coated glass substrate and its current voltage response has been analyzed using Schottky emission theory. The band gap of the material has been calculated using UV visible spectroscopy and found to be 2.7 eV. The current-voltage response of deposited film gives the value of barrier height ($\Phi_b$) and constant factor ($\beta$) as 0.307 eV and 1.89×10^(-4), respectively. These films may have potential applications in electronic and optoelectronic sensing devices.

Keywords: Conducting polymers, Polyaniline, Scanning electron microscopy

Conducting polymers such as polyaniline, polypyrrole, polythiophene etc, have attracted considerable attention for their unique properties and their potential application in a number of growing technologies. Their supremacy is demonstrated by wide range of dependent applications such as electrodes for batteries, energy storage, electrochemical display devices, electromagnetic interference (EMI) shielding, sensors, corrosion protection, organic light emitting diodes, plastic solar cells, optoelectronic devices etc.

Most of the above applications are based on thin film technology. In case of conducting polymers, such films can be easily prepared by chemical/electrochemical polymerisation or by solution processing techniques. In the chemical polymerization process, monomers are oxidized by oxidizing agents or catalysts to prepare conducting polymers. The advantage of chemical synthesis is that it offers mass production at reasonable cost. On the other hand electrochemical method involves the direct formation of conducting polymers with better control of polymer film thickness, internal morphology and minimizing the contamination due to oxidant residues. Solution processing techniques such as spin coating are used to prepare thin films of those polymers which are soluble in a solvent or mixture of solvents. In spin coating process, film thickness and morphology is controlled by spin rate and time of rotation, which make them suitable for use in sensing, electrochromic and other electronic applications.

Polyaniline is so far the most extensively studied conducting polymer due to its ease of synthesis, biocompatibility, good environmental, chemical and electrical stability, good redox properties and moderate electrical conductivity. The charge carriers in polyaniline are generally considered to be polarons and bipolarons stabilised by counter ions incorporated into the polymer during preparation. Therefore, conducting and physical properties of polyaniline depend on the choice of the counter ions, often called dopant. To enhance the processibility of polyaniline, it is usually doped with suitable dopants.

In this paper, we have synthesized polyaniline doped with DBSA and investigated its properties in thin films. We did calculate the band gap of spin coated DBSA doped polyaniline film upon ITO coated glass using UV-visible absorption spectroscopy. The surface morphology and structure of the film were studied using SEM and X-ray crystallography, respectively. FTIR of the sample has also been done to study the formation of the conducting polymer. The electrical transport property...
was also studied and was analyzed in terms of Schottky equations to evaluate the values of potential barrier and constant factor.

**Experimental Procedure**

Aniline (E-Merck India) was double distilled before use where as all other chemicals were of analytical grade and used without any further purification. Double distilled water having conductivity less than $10^{-6}$ Ohm$^{-1}$ cm$^{-1}$ was used for synthesis.

The doped polyaniline (PANI) was prepared by chemical oxidative polymerization following direct approach and using DBSA as a surfactant dopant$^{11}$. 0.1 M of aniline and 0.3 M DBSA were mixed in 1.0 L of distilled water. The mixture was homogenized using high speed blender (ART MICCRA D8) rotating at 10800 rpm for about 30 min to uniformly disperse the phases to form an emulsion. The emulsion was then transferred to double walled glass reactor and cooled to -5°C under constant stirring. The polymerization was initiated by the drop-by-drop addition of ammonium peroxydisulfate (0.1 M, (NH$_4$)$_2$S$_2$O$_8$ in 100 mL distilled water) and the temperature was maintained at -5°C. After complete polymerization (6 h) a dark green emulsion was obtained. Isopropyl alcohol was added to the above emulsion and stirring was continued for another 2 h after which the reaction mixture was filtered to separate the polymer. The wet polymer cake was dried under dynamic vacuum till constant weight and then crushed to obtain the powder of polyaniline$^{6-10}$.

Thin film of DBSA doped polyaniline upon ITO coated glass has been prepared using spin coating technique at the fix spin rate and time by spin coating unit SCU-2007. Filter solution of the material in CHCl$_3$ has been used to prepare thin film upon properly cleaned ITO coated glass. Aluminum was coated on the DBSA doped polyaniline film via thermal evaporation in a vacuum chamber at a base pressure of $1\times10^{-6}$ Torr. Evaporation of Al in high vacuum, minimized the possibility of formation of Al$_2$O$_3$.

The DBSA doped polyaniline film was characterized by UV-visible spectrophotometer (Shimadzu UV-1601), X-ray diffractometer (Bruker, D8 AXS) and FTIR spectrometer (Nicolet 5700). The surface morphology was studied using SEM (Carl-Zeiss, UK).

**Results and Discussion**

The X-ray diffraction (XRD) pattern of spin coated polyaniline film (Fig. 1) gives a broad peak at 25° that is due to the presence of doped polyaniline and matches with the XRD of amorphous polyaniline$^{11-13}$.

Figure 2 shows the FTIR spectra of spin coated polyaniline film upon ITO coated glass in the wavenumber range of 500-2000 cm$^{-1}$ and under transmission mode. The spectra give distinct and prominent bands at 1565.5, 1474.2, 1299.5, 1241.9, 1120.8 and 795.8 cm$^{-1}$ corresponding to different inter-atomic stretching and bending vibrations. In particular, the peak at 1556.5 cm$^{-1}$ may be assigned to C=C stretching vibration of the quinoid ring where as stretching vibration of C=C of the benzenoid ring occurs at 1474.2 cm$^{-1}$. The peak at 1299.5 cm$^{-1}$ is the C-N stretching vibration. The peak corresponding to

---

**Fig. 1–X-ray diffractogram of PANI DBSA**

**Fig. 2–FTIR spectra of PANI DBSA**
1241.9 cm\(^{-1}\) may be assigned to asymmetric C-N stretching modes of benzenoid ring where as the absorption band around 1120.8 cm\(^{-1}\) (C-N stretching) is due to the charge delocalization over the polymer backbone. Similarly, the prominent band at 795.5 cm\(^{-1}\) may be attributed to C-H out of plane deformation. All bands confirm the formation of DBSA doped polyaniline.

Figure 3 shows the SEM micrographs of spin coated polyaniline films at different resolutions. At lower magnification level (Fig. 3(a-c)) some spherical plus elongated particles can be identified. However, higher magnification image (Fig. 3d) shows that diameter of spherical particles lies in the range 50-100 nm whereas elongated particles are 200-300 nm in length and 50-100 nm in diameter. As the nanoparticles possess novel properties which are not present in their bulk counterparts, therefore, enhanced optical and electronic response is expected.

Figure 4 shows the UV-vis spectra of spin coated polyaniline film revealing the presence of two distinct peaks at 749 nm and 357 nm with a shoulder around 450 nm. The lowest wavelength peak (357 nm) corresponds to band-gap transition whereas remaining two transitions represent characteristic features of polaronic states. In order to evaluate the optical band gap of the spin coated films, a graph was plotted between parameter \((A)^2\) and incident energy \((h\nu)\) which are related by Tauc relation:
where $h$ is Plank's constant ($6.67 \times 10^{-34}$ Js), $\nu$ is frequency of radiation, $A$ is absorbance and $E_g$ is optical band gap. The value of $E_g$ was obtained by extrapolating the straight line portion of the $(A)^2$ versus $h\nu$ plot. The intersection of above line with x-axis ($h\nu$ in our case) gives the band gap ($E_g$) of the film\textsuperscript{17}. The results (Fig. 5) shows that optical band gap ($E_g$) of spin coated polyaniline film is 2.7 eV which may be useful for finding applications in electrochromic and optoelectronic devices.

The current voltage ($I$-$V$) characteristic\textsuperscript{18-20} of the thin film of spin coated polyaniline (PANI-ED), was investigated by Kethiley–2400, in the device configuration aluminum/polymer/ITO and the results are shown in Fig. 6. These $I$-$V$ characteristics could be explained by Schottky emission theories and seem to follow the relations:

$$J = A T^2 \exp \left[ \frac{-\phi_B + \beta \sqrt{F}}{kT} \right]$$

...(2)

$$\log J = \left( \log A T^2 - \frac{\phi_B}{kT} \right) + \frac{\beta \sqrt{F}}{kT}$$

...(3)

where $J$ is current density, $T$ is absolute temperature, $\phi_B$ is potential barrier, $\beta$ is constant factor, $F$ is electric field and $A$ is a constant. The plot of $\ln J$ versus $\sqrt{F}$ gives a straight line (Fig. 7). Therefore, potential barrier ($\phi_B$) and constant factor ($\beta$) were calculated from the slope of the curve. The above equation also revealed that the intercept is equal to $\log A T^2 - \phi_B / kT$ whereas slope is $\beta kT$. Therefore, the calculated value of potential barrier ($\phi_B$) and constant factor ($\beta$) were found to be 0.307 eV and $1.89 \times 10^{-4}$, respectively. Such low barrier heights indicate their potential usefulness for electronic applications.

**Conclusions**

Polyaniline has been synthesized successfully via chemically oxidative polymerization in the presence of surfactant dopant DBSA. The FTIR spectra gives the characteristic bands corresponding to stretching and bending vibrations of polyaniline (PANI) and confirms the formation of PANI in the process. XRD
pattern of the DBSA doped PANI gives a broad peak which shows that formed PANI was amorphous in nature. SEM images provide the information regarding the morphology of the material which confirms the formation of nano-sized polyaniline particles. The UV-visible spectra give peaks at 749 nm, 450 nm and 357 nm with characteristic band gap of 2.7 eV. The current-voltage ($I-V$) characteristic of these spin coated DBSA doped PANI films obeyed Schottky emission theory which gives the calculated values of barrier height and constant factor as 0.307 eV and $1.89 \times 10^{-4}$, respectively. The smooth $I-V$ response, moderate band gap and good nano-scale morphology of synthesized DBSA-doped polyaniline film demonstrate its use in optoelectronic devices for sensing applications.

Acknowledgement

The authors are thankful to Director CSIR-NPL for providing the research facilities. The authors are grateful to Dr K N Sood for SEM micrographs & Dr R P Pant for XRD measurement of the samples. Authors are also obliged to Dr M N Kamalasanan for the measurements of I-V characteristics of the sample.

References