Indian Journal of Pure & Applied Physics
Vol. 52, July 2014, pp. 486-490

RF plasma polymerization and electrical, optical and structural properties of thin films of poly(*o*-toluidine)

Shama Islam[1], G B V S Lakshmi[2], M Zulfequar[1], M Husain[1] & Azher M Siddiqui[1]*

[1]Department of Physics, Jamia Millia Islamia, New Delhi 110 025, India

[2]Material Science Group, Inter University Accelerator Centre, New Delhi 110 067, India

*E-mail:-amsiddiqui@jmi.ac.in

Received 25 September 2013; revised 13 December 2013; accepted 20 February 2014

Thin films of poly(*o*-toluidine) (POT) have been prepared by *RF* plasma polymerization at radio frequency (*RF*) power input 15 W, making suitable modifications in a *RF*-sputtering set-up. The deposition rate is found to be 3.33 nm/min. The films are characterized by *dc* conductivity, UV-Visible, FTIR and XRD techniques. The *dc* conductivity of the POT thin films has been analyzed in the temperature range 312-435 K and is found to increase with temperature. The Arrhenious plot of *dc* conductivity shows straight line behaviour. The optical band gap has been estimated to be 1.66 eV from UV-visible absorption spectrum. From FTIR, the formation of POT has been confirmed. It is found that the synthesized polymer is cross-linked. Thickness of the polymer films has been measured to be 200 nm by ellipsometry. XRD shows the amorphous nature of the prepared films.

Keywords: *RF*-plasma polymerization; Poly (o-toluidine); *dc* Conductivity; FTIR; UV-Visible absorption spectrum

1. Introduction

In the past few decades, the synthesis and characterization of conductive polymers have become one of the most important research areas in polymer science. These polymers have applications from insulators to superconductors showing excellent electrical, optical and optoelectronic properties. The composition, morphology and physical properties of these polymers differ in each case, which depend on the polymerization and reaction conditions. Traditionally, these polymers are synthesized via chemical and electrochemical polymerization. Recently, plasma polymerization is recognized as another important method to obtain thin films of conductive polymers[1-5]. The chemical structures of plasma polymerized conductive polymers are rather different from conventional polymers and dependent on the plasma polymerization conditions[6,7]. Plasma polymerized conductive polymer films have been characterized as high quality, adherent, pinhole free and branching. Under plasma conditions, non-specific and very complex chemical reactions occur. By free radical mechanism, glow discharge polymerization of organic compounds proceeds[8-10] and the extent of ionization is small. The combination and recombination of these radicals form high molecular weight compounds, which are polymers[11]. Input power, monomer rate and deposition time affect the morphology, thickness and structural properties of these films[12]. The electrical and optical properties of POT as blends and fibers have already been studied[13-15]. The methyl-substituted aniline called *o*-toluidine has been found to have additional advantage over polyaniline due to its fast switching time between the oxidized and reduced states. POT is found to be the most promising because of its ease of synthesis, low cost monomer, tunable properties, and better stability as compared to other intrinsically conducting polymers. Hence, the systematic studies on the synthesis, characterization and applications of POT have been carried out in the present paper[15,16]. It can be ascertained at this juncture that the thickness and orientation of polymeric molecules play an important role on the electro activity of POT film[17,18]. In general, polymer films are of great importance due to their increased industrial applications as electrodes and membranes for electrochemical energy conversion and storage, organic diodes. Plasma polymerized thin films find innumerable applications ranging from corrosion free adhesive coating materials to sensor technology and microelectronics.

In the present work, the new design of a set-up to achieve maximum deposition on the substrates in the modified chamber has been reported. In an existing

RF-Sputtering unit; this is a set-up for position of vaccum inlet, *RF* generator, Ar inlet and controlled inlet of monomer vapours in the unit, to achieve maximum deposition. The synthesis and characterization of plasma polymerized POT films have been presented. The mechanism of *RF* plasma polymerization of POT films, the general aspects of polymerization of aniline and its derivatives by this method have also been investigated. The films are characterized by *dc* conductivity, UV-Vis spectroscopy, FTIR, XRD and ellipsometry.

2 Experimental Details

Plasma polymerized thin films of (o-toluidine) on ultrasonically cleaned glass and silicon wafer substrates were obtained by polymerizing of (*o*-toluidine) monomer (99.9% purity) under radio frequency (*RF*) plasma discharge in a home built set-up. This is a custom-manufactured glass deposition chamber, coupled to a vacuum system, *RF* amplifier and a monomer feed-through set-up. For maximum deposition, a novel set-up has been designed. The position from where evacuation take place and the position of monomer feed through are crucial in this set-up; a schematic which is shown in Fig. 1. Feed-through set up consists one on/off valve and one needle valve. The on/off valve is to create a quick vacuum in monomer pot and needle valve regulates the flow of monomer vapours into the chamber. This helps us to achieve maximum deposition rate on substrates[19,20]. The monomer vapours enter slowly in to the chamber through needle valve. During a typical experiment, the glass and silicon substrate are placed on the lower electrode.

The system was evacuated to lower than 10^{-3} torr and argon gas was introduced into the chamber for plasma pre-treatment for 20 s. The *RF* power applied was 15 W for about 1 h. Fragmentation of monomer takes place because of the Ar plasma created between the electrodes. The deposition rate is estimated to be 3.33 nm/min under constant deposition conditions; the thickness of the film is estimated to be 200 nm by ellipsometry. FTIR has been carried out by using NEXUS-670 FTIR spectrometer of thin films of POT, deposited on Si substrate (polished from both the sides). X-ray diffraction (XRD) studies have been carried out by using a Panalytical (PW 3710) X-ray powder diffractometer with Cu Kα radiation. The sample is scanned in angular range of 0-70° with scan speed of 0.01°/s under similar conditions. UV-Vis spectroscopy of the samples has been carried out using Camspec M550 double beam UV-Vis Spectrophotometer.

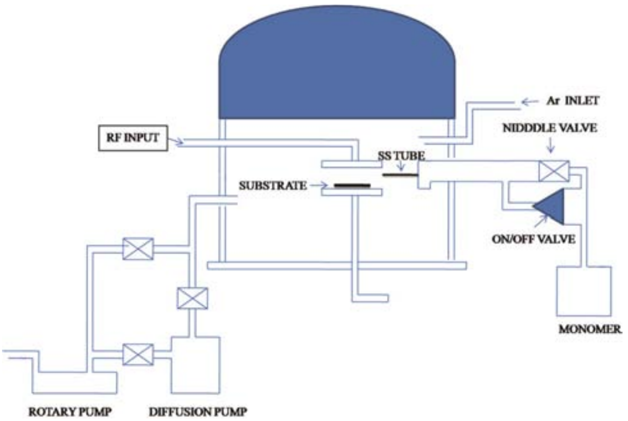

Fig. 1 — RF-plasma polymerization set-up

3 Results and Discussion

3.1 dc conductivity studies

The *dc* conductivity of *RF* Plasma polymerized thin films has been studied in temperature range 312-435 K at a constant voltage of 1.5 V and pressure of about 10^{-3} torr. The resultant current was measured with a pico-ammeter. For semiconducting materials, the *dc* conductivity can be expressed by Arrhenius relation:

$$\sigma_{dc} = \sigma_0 \exp\left(\frac{-\Delta E_a}{kT}\right) \quad \ldots(1)$$

where ΔE_a is the activation energy, σ_o the pre exponential factor related to the material, *k* Boltzmann constant and *T* is the temperature. The Arrhenious plot of conductivity versus temperature shows a good straight line behaviour, implying that the charge transport is mainly by band conduction (Fig. 2). The value of the activation energy (ΔE_a) is estimated with the help of the slope of lnσ versus 1000/*T* plot. The slope of the curve is estimated by using the linear fit[21-23]. The plasma polymerized thin film of POT shows a higher conductivity (1.65×10^{-9} S/cm); this may be due to the fact that during *RF* plasma polymerization, a large amount of energy is deposited on the target system within a small period of time along the ion path (track).

The energy is so high that it can break all the chemical bonds along the track. The energy dissipates to the surrounding regions within a few nanoseconds. This energy leads to bond breaking, chain scissoring, cross-linking, radical formation, etc., which in turn cause molecular rearrangements in the polymer. Collective excitation (plasmons), which produces a large excited volume resulting in coercive interaction among the ions and radical pairs produced in the adjacent chains within the volume as a result of an electron stopping mechanism, is responsible for cross-linking of the polymer chains. Inter-chain electron hopping required for conduction between two chains is facilitated due to the cross-linking of the polymer chains after *RF* plasma polymerization. Defect sites in the molecular structure of the polymer chain created by *RF* plasma polymerization also contribute to higher *dc* conductivity as charge accumulation takes place, which produces charge carriers. In POT, the dominating charge carriers are polarons and bipolarons[24-26].

3.2. UV-Visible studies

The UV-Visible absorption spectra show the variation of optical density with wavelength of the incident photon (Fig. 3). The broadening of absorption peak shows the increase in conjugation and the widening of spectrum of the polymer films. From the absorption spectrum, the optical band gap has been measured using Tauc's relation[18,19,23]:

$$(\alpha h\nu) \propto (h\nu - E_g)^n \text{ where } n=1,2,3,\ldots. \qquad \ldots(2)$$

The index n has discrete values like 1/2, 3/2, 2 or more depending on whether the transition is direct or indirect and allowed or forbidden, respectively. In the direct and allowed cases, the index n is 1/2 whereas for the direct but forbidden cases it is 3/2. But for the indirect and allowed cases n=2 and for the forbidden cases it will be 3 or more. The present system obeys the rule of indirect transition with n=2. α is given by:

$$\alpha = O_d/t \qquad \ldots(3)$$

where O_d is the optical density measured at a given film thickness (t) and the extinction coefficient (k) is given by:

$$k = \alpha\,\lambda/\,4\pi, \qquad \ldots(4)$$

where λ is wavelength of incident photon. The peak around 335 nm is attributed to strong inter band n–π^* transition, due to excitation in the aromatic ring. The other humps in the graph are attributed to π–π^* transitions[27,29].

The optical band gap is determined from the absorption spectrum. The value of k estimated at 325 nm is around 0.06. The optical band gap energy (E_g) can be obtained by plotting $(\alpha h\upsilon)^{1/2}$ versus ($h\upsilon$) and extrapolating the linear portion of $(\alpha h\upsilon)^{1/2}$ to zero. The allowed indirect transition optical gap is found to be 1.66 eV for the POT films.

3.3 FTIR and XRD Studies

The FTIR spectrum of POT film prepared on Si substrate shown in Fig. 4. This spectrum exhibits the following main spectral features. The band at 1619 cm^{-1} can be assigned to the C-C stretching mode

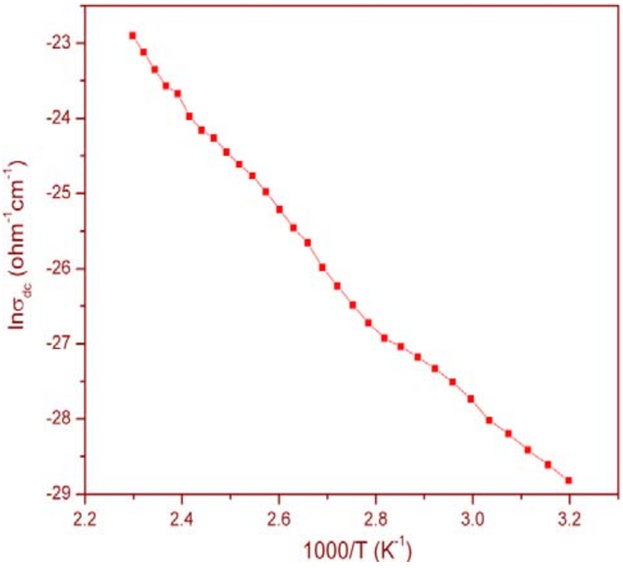

Fig. 2 — Plot of *dc* conductivity versus 1000/*T* of POT (thin film)

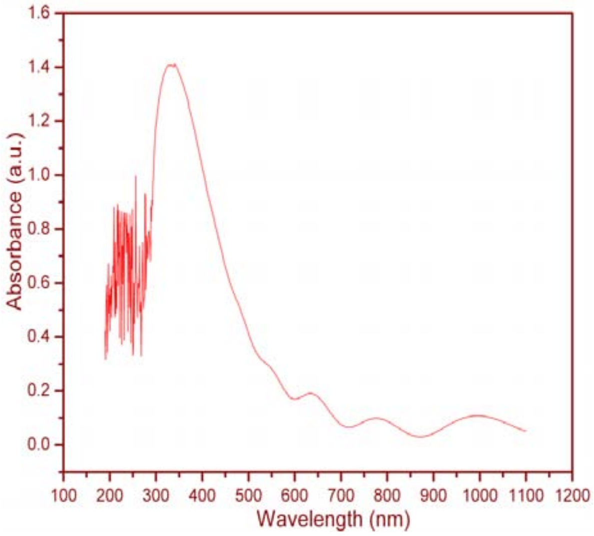

Fig. 3 — Plot of UV-absorption spectra versus wavelength (nm) of POT (thin film)

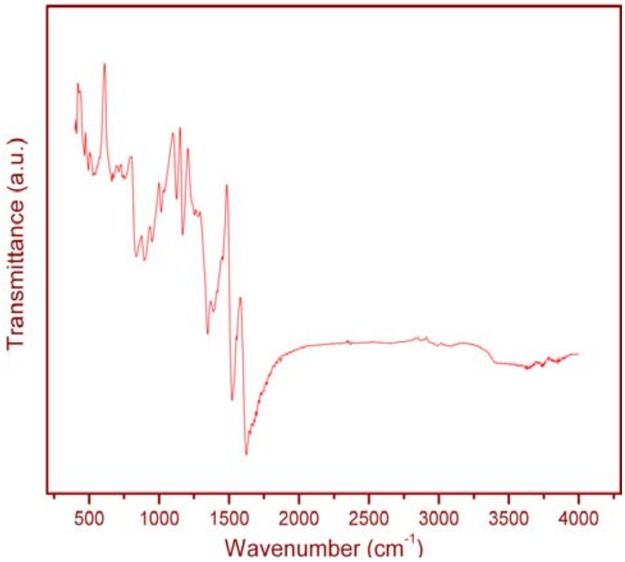

Fig. 4 — Plot of FTIR spectrum of the POT (thin film) prepared on Si substrate

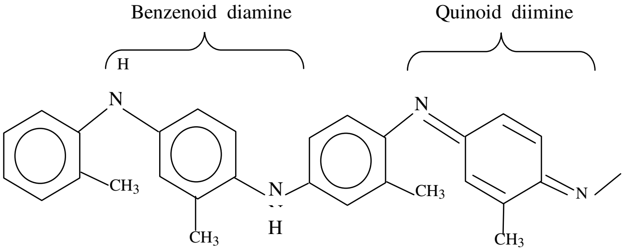

Fig. 5 — Schematic scheme proposed for formation of POT

combined with C=N stretching vibrations of the quinoid rings. The band at 1496 cm^{-1} is attributed to the C-C stretching modes in the benzenoid units. The bands at 1303 cm^{-1} and 1267 cm^{-1} are assigned to the C-N stretching vibrations in the polymer chain. The band at 1146 cm^{-1} is related to the C=N stretching mode. The band at 1034 cm^{-1} can be attributed to charge delocalization on the polymer backbone[29-31]. There are closely spaced weak vibrations present around 1496 cm^{-1} and 1466 cm^{-1} which may be due to the cross-linking of the polymer films.

Hence, it is inferred that the plasma polymerized POT films contain molecular groups due to the fragmentation of the monomer ring. The quinoid and benzinoid rings confirm the polymerization of *o*-toluidine to POT. This is a combination of POT with minor ingredients from other reactions. The scheme of the formation of POT is proposed in Fig. 5.

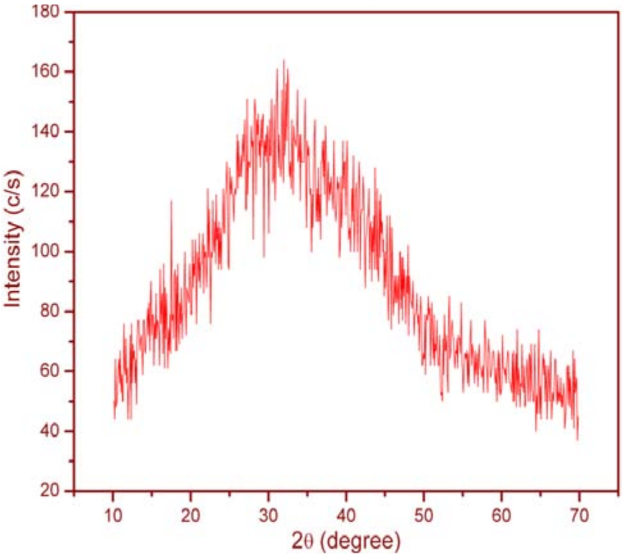

Fig. 6 — Plot of XRD spectrum of POT (thin film)

XRD pattern of POT (thin film) shows the amorphous nature with humps at 25°-40° as shown in Fig. 6.

4 Conclusions

We have successfully deposited POT thin films by *RF* plasma polymerization method without using any carrier gas at a deposition rate of 3.33 nm/min. The *dc* conductivity of POT thin films is found to increase with temperature and conduction which is mainly due to band conduction. The optical band gap of the obtained POT films is found to be 1.66 eV. FTIR spectrum confirms the formation of the cross-linked POT films. XRD shows the amorphous nature of POT thin films.

Acknowledgement

The authors are thankful to Dr Ritu Shirivastava and her group, National Physical Laboratory, New Delhi, for measurement of thickness. Authors are also thankful to Mr Sanjeev Dixit for providing technical support during sample preparation. One of the authors (Shama Islam) is thankful to University Grants Commission (UGC), New Delhi for providing non net fellowship

References

1 MacDiarmid A G, Chiang J C, Halpern M, Mu W L, Somasiri N L D, Wu W & Yaniger S I, *Mol Cryst Liq Cryst*, 121 (1985) 173.
2 MacDiarmid A G, *Synth Met* 8(1997) 427.
3 Neoh, K G, Tan K K, Goh P L, Huang S W, Kang K T & Tan K L, *Polymer*, 408 (1999) 87.

4 Somani P R, Viswanath A K, Aiyer R C & Radhakrishnan S, *Sens Actuators B,* 80 (2001) 141.

5 Somani P R, Viswanath A K, Aiyer R C & Radhakrishnan S, *Org Electron,* 2 (2001) 83.

6 Somani P R, Marimuthu R, Viswanath A K & Radhakrishnan S, *Polym Degrad Stab,* 79 (2003) 77.

7 Boenig H V & Mark H F, Kroschwitz JI (Eds), Encyclopedia of Polymer Science and Engineering, *John Wiley, New York*, 11 (1986) 248.

8 Yasuda H, *Plasma Polymerization Academic Pres, Orlando* (1985).

9 Kumar A & Hussain A M P, *Nucl Instrum Methods B,* 251 (2006) 451.

10 Yasuda H & Hsu T, *J Poly Sci Appl Chem, Ed* 1581 (1977).

11 Gaur S & Vergason G, Technology proceedings of 43 rd Annual Technical Conference Denver (2000).

12 Saravanan S, Joseph Mathai C, Venkatachalam S & Anatharaman M R, *New J Phys,* (2004) 664.

13 Chapman S E, Bilingham N C & Armes S P, *Synth Met*, 995 55.

14 Anand J, Palaniappan S & Sathyanarayana D N, *Synth Met,* 66 (1993) 129.

15 Saini S M, Singh S, Nautiyal L & Auluck S, *Indian J Pure & Appl Phys,* 45 (2007) 66-68.

16 Singh N, Saini S M, Nautiyal T, & Auluck S, *Indian J Pure & Appl Phys*, 45 (2007) 69.

17 Ram, M K, Joshi M, Mehrotra R, Dhawan S K & Chandra S, *Thin Solid Films,* 304 (1997) 65.

18 Borole D D, Kapadi U R, Kumbhar P P & Hundiwale D G, *Mater Lett,* 56 (2002) 685.

19 Kumar D, *Eur Polym J,* 37 (2001) 1721.

20 Macdiarmid G, Mammone R I, Krawczyk J R & Porter S, *J Mol Crys Liq Cryst,* 105 (1984) 89.

21 Gomes M A B & Goncalaves M A, *Electrochim Acta,* 37 (1992) 1653.

22 Wang Y Z, Joo J, Hsu C H & Epstein E T, *Synth Matals*, 68 (1995) 207.

23 Bhat N V & Wavhal D S, *J. Appl Polym Sci*, 70(1) (1998) 203.

24 Akther H & Bhuiyan A H, *New Phys*, 7 (2005) 173.

25 Lakshmi G B V S, Dhillon Anju, Avasthi D K, Zulfequar M & Siddiqui A M, *Eur Polym J*, 45 (2009) 2873.

26 Majeed Khan M A, Zulfequar M, Kumar A & Husain M, *Mater Chem Phys*, 87 (2004) 179.

27 Andrade E M, Molina F V, Florit M I & Posadas D, *J Electroanalytical Chem,* 415 (1996) 153.

28 Ramana C V, Smith R J, Hussain O M, Chusuei C C & Julien C M, *Chem. Mater.*17 (2005) 121.

29 Dilsiz V & Akovali G, *Polymer,* 37 (1996) 333.

30 Lakshmi G BV S, Ali Vazid, Siddiqui Azher M, Kulriya P K & Zulfequar M, *Eur Phys J Appl Phys*, 39(3) (2008) 251.

31 Mathai C J, Saravanan S, Anatharaman M R, Venkatachalam S & Jayalekshmi S, *J Phys D Appl Phys*, 35 (2002) 2206.