Materials Science in Semiconductor Processing 39 (2015) 659–664

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Chemical synthesis and charge transport mechanism in solution processed flexible polypyrrole films

Manish Taunk [a,b,*], Subhash Chand [b]

[a] Department of Physics, Indus International University Una, Himachal Pradesh 174301, India
[b] Department of Physics, National Institute of Technology Hamirpur, Himachal Pradesh 177005, India

ARTICLE INFO

Keywords:
Flexible thin films
Polypyrrole
Charge transport
Variable range hopping
Solution processed polypyrrole

ABSTRACT

Polypyrrole (PPy) has been synthesized by a chemical oxidation method using ammonium persulfate to obtain a solution processable PPy powder. The resultant PPy powder was then solution processed to deposit flexible thin films of PPy over flexible substrates. PPy film samples were then characterized using UV–vis spectroscopy, FTIR spectroscopy and X-ray diffraction. It was found that conductivity of PPy ($\sigma = 2.4 \times 10^{-2}$ S/cm) reduces by an order of magnitude after solution processing in the form of films. The temperature dependent conductivity of PPy pellet and flexible films of PPy were measured in the temperature range of 80–300 K. It was observed that PPy films show stronger temperature dependence than pelletized samples. Charge transport in PPy samples has been investigated using Kivelson's and Mott's variable range hopping models. Mott's parameters such as density of states at the Fermi level $N(E_F)$, average hopping distance (R) and average hopping energy (W) have been estimated for PPy samples. The results showed that at room temperature average hopping distance for PPy film was about 22.3 Å and average hopping energy was 128.6 meV.

1. Introduction

In recent years, conjugated polymer polypyrrole (PPy) have been the focus of intense research due to its particular properties such as high electrical conductivity, good environmental stability and potential for organic electronic applications [1,2]. For widespread applications of PPy in flexible, light weight, low cost fabricated devices such as organic light emitting diodes (OLEDs) [3,4], solar cells [5], supercapacitors [6], polymer batteries [7], microwave shielding [8], sensors [9] and field effect transistors (OFETs) [10] it is essentially required to obtain PPy films through solution processing. PPy obtained by conventional chemical and electrochemical methods is insoluble and infusible [11,12] which limits its extensive use in organic electronic devices. Electrochemical method has size restrictions limited to electrode area. Several attempts have been made in the past to improve the processing and hence application by preparing blends and composites containing conducting PPy [12–15]. In addition to composite preparation, approaches have been reported to increase the solubility by employing long chain counter ions as dopant in the PPy backbone [16–20]. The poor processing ability of PPy is due to strong interchain interactions and by introducing these long chain counter ions in the resultant PPy the interchain interactions becomes weaker and its solubility increases in certain organic solvents. Although a significant decrease in electrical conductivity caused by reduction in π-conjugation of PPy backbone may occur due to an increase in torsion angle between pyrrole rings [21]. Kim et al. [22] synthesized partially soluble PPy using dodecylbenzene sulfonic acid (DBSA) as dopant. The addition of extra amount of DBSA further improves solubility and

---

[*] Corresponding author: Mob: +919418259479.
E-mail address: manishphy@gmail.com (M. Taunk).

http://dx.doi.org/10.1016/j.mssp.2015.06.015
1369-8001/

increase in solubility was attributed to micelle effect. Later similar approaches have been used to synthesize PPy using various long chain sulfonic acids as dopant. Lee at el. [23] reported that oxidant to monomer (O/M) molar ratio plays an important role in determining the solution processing of PPy. They reported that if O/M molar ratio is greater than 0.2, the PPy obtained was insoluble in many solvents. Oh at el. [21] reported synthesis of solution processed PPy by employing bis(2-ethylhexyl) sulfosuccinate sodium (NaDEHS) as dopant and reported better solubility and also appreciable value of conductivity in solution processed films.

The charge transport studies over wide range of temperature in these chemically synthesized using NaDEHS and solution processed PPy films are scarce [20]. It is worthwhile to study and understand charge transport properties in these PPy films before their potential use in precisely controlled device applications. Despite of a large number of studies, charge transport mechanism in conducting polymers (CPs) still remains a topic of discussion and research [24–29]. This is probably due to the different type of structural and electronic defects as well as lack of long range ordering, which arises during synthesis. The conduction mechanism in amorphous materials such as PPy is primarily governed by hopping of carriers from one localized state to another, randomly distributed in space and energy. First model to explain conduction in CPs was proposed by Kivelson wherein the charge transport occurs between neutral and charged solitons at iso-energetic levels [30]. Later this model was modified for interpolaron hopping conduction in case of non-degenerate ground state CPs [31]. The other model which is universally accepted and employed to explain charge transport mechanism in various disordered semiconductors is Mott's variable range hopping model (VRH). In a strongly localized system charge carriers hop to the nearest neighbor state however in weakly localized system, the charge carriers' hop to the sites for which the required activation energy is small and resides farther away. This type of hopping conduction is known as variable range hopping [32].

In the present work, we reported synthesis of solution processable PPy by chemical oxidation method. PPy powder thus obtained is then used to deposit thin films on flexible substrates by solution casting method. The advantage of solution processable PPy is that it can be deposited on any substrate. The PPy films were then characterized using FTIR, XRD and electrical conductivity measurements. Electrical conductivity was measured in the temperature range of 80–300 K for both PPy pellets and solution processed films on flexible substrate. The measured data of both samples have been analyzed in the light of hopping conduction mechanisms.

2. Materials and methods

PPy has been synthesized by chemical oxidation method. Pyrrole monomer (Spectrochem), NaDEHS (Alfa aesar) and ammonium persulfate (APS, Alfa aesar) were used as starting material. Methanol of reagent grade was procured from Merck. In these reactions NaDEHS was dissolved in the 150 ml cooled (~0 °C) de-ionized water under magnetic stirring. The pyrrole monomer was added to this solution and then stirred magnetically for about two hours. APS was dissolved in 50 ml de-ionized water and this precooled (~0 °C) solution was drop wise added to cooled aqueous solution of pyrrole and NaDEHS under continuous magnetic stirring. The polymerization reaction was carried out for about 20 h at ~0 °C under continuous magnetic stirring. The oxidant to monomer ratio in this reaction was fixed at 0.2 and dopant to monomer ratio was fixed at 0.4. For precipitation to occur methanol was added to the reaction medium and after six hours the precipitated PPy was collected by filtration. The collected precipitates were then washed in excess de-ionized water and methanol to remove unreacted traces and oligomers formed. The wet precipitates were then dried inside vacuum oven at 50 °C for about 24 h to get the constant weight dried polypyrrole powder.

To determine the solubility of PPy obtained a calculated quantity of PPy was dissolved in dimethyl formamide (DMF) under magnetic stirring for an hour. It was observed that 25 mg of dried PPy powder gets completely dissolved in 5 ml of DMF and a homogeneous solution was formed without any undissolved particles remaining in solution. This homogeneous solution was then casted on OHP (overhead projector) sheets having area (4×4) cm^2 and solvent was allowed to evaporate inside the vacuum oven for about 12 h at 50 °C. The films were then dried for another 6 h at 60 °C under vacuum. Thickness of the solution casted PPy films was found to be ~1 μm. Image of solution casted PPy films on flexible OHP sheet are shown in inset of Fig. 3. These films have been further characterized using UV–vis spectroscopy, FTIR, XRD and conductivity measurements. Conductivity was calculated using the relation $\sigma=(0.2206/t)(I/V)$ where, t is the thickness of the sample, I is current applied through the outer probes and V is the voltage measured across inner probes. Schematic of four probe setup is shown in inset of Fig. 4. The four probe setup consists of a current source (Keithley 2400 source meter) and a nanovoltmeter (Keithley 2182A) for voltage measurement. All measurements were performed in a vacuum sealed cold head by passing current continuously through the samples.

3. Results and discussion

Polymerization yield obtained in this reaction was 35% and conductivity of PPy powder was 2.4×10^{-2} S/cm. The conductivity of PPy powder was measured in the form of compressed pellets having thickness 1mm and diameter 13 mm. In solution processed films conductivity was found to be 2.6×10^{-3} S/cm. It was revealed that after solution processing of PPy films, conductivity reduces to one order of magnitude. This conductivity reduction was due to strong interaction between the PPy chains and solvent perturbing the molecular interaction between PPy and dopant. Such type of behavior is also reported for PPy-DBSA films [33].

3.1. *UV–vis spectroscopy*

The PPy-DEHS solution in DMF showed a strong and sharp absorption maximum near UV region at 410 nm and comparatively weak and broad absorption peak in the