Solvent induced charge transport mechanism for conducting polymer at higher temperature

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Abstract
To elucidate the response of different solvents such as isopropyl-alcohol (IPA) and acetone for polyaniline-emeraldine-base (PANI), the charge transport mechanism is investigated as a function of temperature in the presence of different solvents. From SEM and XRD characterization, it is noted that each solvent improves the surface smoothness and negligible solvent traces were observed in the final thin-film devices. It is further observed that all devices follow space-charge-limited-current (SCLC) model to define their electrical responses. Conductivity was measured directly through four-probe method, while mobility was estimated from SCLC model and then both conductivity and mobility of PANI are compared with the given solvent at different temperatures. Similarly, it is also realized that the IPA solvent improves conductivity, mobility and degradation of PANI thin-film due to complex behaviour of solvent induced self-organization of molecular chains and reduction of residual traps as a function of temperature.

1. Introduction
Poly-Aniline-emeraldine-base (PANI) is an excellent conducting polymer, which can be easily processed and doped by using commonly available acids, dyes and many other types of dopants [1]. According to the reported literature, conducting polymers are usually deposited over substrate for electronic devices by solution-processing method, which requires proper solvent for highly efficient electronic devices [2–33]. Solvent not only assists solution-processing but also enhances the electrical conductivity of conducting polymers as secondary doping [2, 3]. For most of conducting polymers, solvent plays a key role throughout solution evaporation process during thin-film spin-coating deposition.

Both solvents isopropyl alcohol (IPA) and acetone have capability to dissolve a wide-range of organic and non-organic semiconductor materials for thin film deposition and they evaporate very quickly with negligible traces after spin-coating process compared to other solvents [4]. Similarly the IPA and acetone are considered as best green solvent as they offer very low toxic responses. At the same time, IPA and acetone are also biodegraded very easily and efficiently, therefore they are not very harmful for our ecological environment. On the other hand both solvents play some vital role for further improvement in many aspects of electronic devices, therefore many researchers are using these green solvents for thin film deposition especially for organic and pervoskite materials [4–9]. Recently Kim et al reported the significant improvements in polymer light emitting diode response by using IPA solvent for PEDOT:PSS as hole-transport layer [5]. Chen et al reported novel energy storage characteristics of polyaniline based form stable phase change materials (PCM), which were prepared by using IPA by a simple method [6]. Moiz et al observed the improved dispersion of silver nanoparticles inside PANI in the presence of IPA and acetone [7, 8]. Similarly, Samawati et al fabricated highly sensitive and commercially viable polymethyl methacrylate polymer based optical fiber sensor by using acetone as solvent [9].

For conducting polymer PANI, different solvents have already been reported for their thin-film deposition, and here we have selected IPA and acetone on the basis of above discussion. As pure PANI has very low electrical conductivity for many electronic applications, therefore the conductivity of PANI is improved by primarily
doping with poly-acrylic-acid (1:1, PAA) for all samples and then further doped by either using solvent IPA, or acetone [13, 16]. Since, in this study we are mainly interested for comparative analysis of PANI with different solvents, therefore we tried our best to develop all these samples at the same time and under the same laboratory environments with same standard procedures.

Generally, it is accepted that the settling time of polymer molecular chains during solvent evaporation process either enhance or degrade the overall electrical characteristics of polymer thin films [7]. But unfortunately, the direct measurement and evaluation of molecular settling time regarding the solvent evaporation process is still very complex for many applications [10, 11]. During the solution-processing of thin film, the unsuitable solvent molecules are confined and surround the polymer molecular-chains and degrade the electrical responses even after performing post annealing process [7, 12, 13]. By and large these confinements are the main source of electronic traps for charge transport conduction through-out the polymer chain. The nature of these confinements are the strong function of temperature as well as solvent used. Generally low boiling point solvents such as IPA and acetone improve the order of polymer chains and hence crystallinity of PANI thin film during evaporation stage of spin-coating process as a result conductivity is increased. Solvent induced improvements in polymer chains are further enhanced at higher temperature due to lowering of electronic traps offer to the free carrier density especially under the influence of applied voltage. These electronic traps have direct impact on charge transport parameters, such as mobility and conductivity and therefore it is very crucial to determine the behaviour of traps in the presence of solvent as a function of temperature not only from fundamental but also from technological point of view [14, 15].

Therefore, in this study, the effect of temperature ranging from 0 °C to 60 °C for electrical properties of freshly prepared PANI diodes as devices with solvent such as isopropyl alcohol (IPA) and acetone were investigated and discussed.

2. Experimental

2.1. Device fabrication

For this study, all chemicals such as PANI (Mw 50,000 gm/mole), poly-acrylic-acid (PAA), IPA and acetone were purchased from Sigma-Aldrich and were used without any further purification. Similarly 2 \times 2 cm² aluminum pre-coated glass substrate was purchased from local market and washed with detergent, deionized water, IPA/acetone respectively and then soaked with inert nitrogen before used.

For polymer solution, 10% of PANI by weight solution was mixed either in IPA or acetone solvent and magnetically hot-plate stirred for more than 8 h continuously. After solution formation, thin film of PANI, PANI-IPA and PANI-acetone was deposited on 200 nm pre-coated aluminium thin film over glass substrates by spin-coating method with 1500 rpm for ~30 s approximately. For metalization, Ag thin films were deposited on to the top of PANI as well as Al surface through vacuum evaporation method, where chamber pressure was maintained 1 \times 10^{-6} Torr during the Ag thin-film deposition process. Polymer as shadow mask were clipped over the top of the device to define the four equal-distance collinear metallic probe contact areas (10 \times 10 mm²) for Ag thin film deposition. The Thickness of Ag thin film was monitored and measured (100 Å) through in situ quartz crystal microbalance method (QCM). The finished samples were then annealed at 100°C for 3 h in the inert atmosphere of nitrogen. The cross-sectional diagram of the finished devices is shown in figure 1.

2.2. Characterization

Surface characterization and PANI thin-film thickness for all devices was measured by scanning electron microscopy (FE-SEM; JEOL JSM-6330F) and was found in the range of 5.8 ± 0.3 μm.

Current-voltage characteristics were measured with the help of HP4145B parameter-analyzer for each sample by using automatic-control dark-box with temperature adjusting facility, where measured temperature error was found in the range of approximately ±0.5 K for given experiments. For electrical characterization as well as conductivity measurement the input voltage (V) is applied between two outer electrodes and the resulting current is measured between two inner probes as shown in figure 1.

The X-ray diffraction (XRD) patterns of PANI thin-films with or without solvent was measured with the help of D/MAX 2000 V diffractometer, Rigaku, Japan by using monochromatized Cu Ka radiation with scanning rate 40 per minute.

3. Result and discussions

The microstructure and surface morphology of PANI is effected by the nature of solvent during solution-processing. Therefore, the surface morphology of (a) PANI, (b) PANI + IPA and (c) PANI + Acetone thin film deposited over Al electrode is characterized by scanning electron microscopy (SEM) and shown in figure 2. All
Figure 1. Cross-sectional diagram of the sample used for electrical characterization, where PANI thin film with either IPA or acetone deposited over Al thin film electrode. For electrical characterization four equal distance Ag electrodes were deposited, where input voltage ($V$) is applied between two outer electrodes and the resulting current is measured between two inner electrodes.

Figure 2. SEM images of (a) PANI (b) PANI + Acetone (c) PANI + IPA.
SEM images explicitly demonstrate that the various size of granules are irregularly spread over the entire surface of PANI thin-film. The widespread cauliflower like granules with full of porosity formed the amorphous layered structure of molecular chains. Molecular chains play a vital role to define the electrical response of PANI. These granules, porosity and layered molecular structures are enhanced in the presence of acetone in PANI + acetone film, but much enhancement is identified with IPA solvent in PANI + IPA film which cause to improve the amorphous structure and surface smoothness of PANI as shown in figure 2.

In order to investigate the crystalline structure and the presence of IPA and Acetone traces in PANI thin film, the XRD analysis of (a) PANI, (b) PANI + IPA and (c) PANI + Acetone was performed, and their patterns are presented in figures 3(a)–(c) respectively. All these XRD patterns reveal that (a) PANI, (b) PANI + IPA and (c) PANI + Acetone are purely amorphous in nature, where the much broader peak for all XRD patterns at 2θ close to 24 is associated to the diffraction of amorphous PANI. Similar XRD patterns are observed for all above samples and there is no prominent solvent peak associated with any XRD pattern. So it can be deduced from above patterns that due to the solvent evaporation process during spin-coating based thin-film formation as well as annealing of the device at 100 °C for 3 h after thin film deposition, the most traces of solvents were evaporated (boiling point of acetone, IPA are 85.5 and 56 °C respectively).

For electrical characterization, current-voltage (I-V) responses were measured for each device from temperature range 0 to 60 °C. Figure 4, shows the logarithmic current (Log I) as a function of applied voltage (V) for (a) PANI, (b), PANI + IPA solvent, and (c) PANI + acetone solvent respectively. It is clear from the figure that, at low applied voltage typical ohmic behaviour is observed and then ohmic behaviour leads to the trap filling spaced charge regime and finally pure space charge regime is observed at higher applied voltage for all devices. The space charge limited current density (J) in the presence of traps can be defined as

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu_0 V^2 \Lambda^3$$

(1)

Where $\varepsilon_r$, $\varepsilon_0$, $\mu$, $V$, $L$ and $\theta$ are the dielectric constant of polymer, dielectric constant of free space, carrier mobility, applied potential, thickness of film and trap factor for polymer respectively. Conductivity for each sample was measured separately with four-probe method as shown in figure 5 and these results are found in great agreement with measured conductivity from I–V characteristics. Figure shows that all samples follow Arrhenius equation for conductivity ($\sigma$) as a function of temperature (T) which can be written as

$$\sigma = A e^{-E_a/kT}$$

(2)
Where $\sigma_o$, and $E_a$ are the pre-factor and activation energy respectively and are interrelated to each other according to Meyer-Neldel rule, correlated with the distribution of trapping sites inside the conducting polymer.

As Chung and many other researchers had found that traps parameters estimated from mobility measurement either from SCLC model or time of flight (TOF) method are very close to each other [12, 21], therefore, just for simplicity we measured the mobility from SCLC model as a function of temperature by standard method as shown in figure 6 [31]. The mobility of all PANI samples are relatively insignificant at low temperature and then sharply rises and becomes substantial specially for PANI-IPA as compared to PANI-acetone device at higher temperature, which is typical behaviour and commonly observed for many disordered polymer semiconductor [22, 23]. In order to disclose the relation between polymer disorder and solvent impact, the trap density is measured. As trap density ($N_T$) is a direct function of trapped filled voltage ($V_{TFL}$), therefore, we derived $N_T$ from equitation 1 and can be written as [22, 23].

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right)$$ (2)
As $V_{TFL}$ depends on temperature, therefore $N_T$ also depends on temperature and were calculated from equation (3) for given temperature range. Similarly, with the help of SCLC equation [31], the trapped carrier density were also calculated as a function of temperature and are shown in figure 7. From the figure it is clear that at region I, trapped carriers density is very high for all samples and then the trapped carrier density decreases and become the part of free carrier density due to thermal activation as shown in region II of figure 7.

At very low applied electric field solvent induced self organization of chains may be ineffective as compared to the solvent induced disorder reduction as well as the chain deformation traps [26]. Therefore, at low electric field the improvement in mobility for PANI, PANI-IPA and PANI-acetone is negligible due to lack of solvent induced chain conformation and residual traps improvement, while mobility of all samples is increased at higher temperature caused by the thermal activated diffusion process of the free charges ($E \approx 0$) inside the polymer. As solvent-induced-traps reductions are more pronounced with IPA, therefore mobility of IPA is significantly higher than mobility of acetone at higher temperature.

At higher electric field, the straightening of polymer chains may causing C-C single bond to shrink and C-C double bond (pi-bond) to expand, which provide higher conjugation length cause to improve the conductivity and mobility of the conducting polymer(see figures 4 and 5) [25]. Therefore, in the presence of electric field with a function of temperature the mobility (and conductivity) is greatly influenced by temperature dependent.
behaviour of field and solvent induced self-organization and traps dynamics \cite{7}. From figures it is clear that mobility and conductivity of PANI-Solvent is higher than PANI, therefore it can be concluded that field and solvent induced self-organization is dominated over the traps dynamics and cause to improve the overall conductivity and mobility of PANI. Since all these factors are function of temperature, therefore, their general behaviour is very complex function of temperature as shown in figure. At both region I and II, field induced self-organization is same for both PANI-solvent sample. But solvent encourages self-organization of PANI, and is different due to different boiling point of solvents. On the other hand, solvent also changes the polymer chains from compact to extended states and causes to de-localize the charge carriers and improves the inter-chain transport and conductivity of polymer even in the presence of higher trap density. Now, we discuss the different behaviour of PANI-solvent in both regions. As IPA offers more traps density in region I (high boiling point) therefore, the conductivity and mobility of PANI-acetone is higher in the region I, when temperature is further increased then due to thermal activation polymer chain become more extended with IPA as compared to acetone, hence causes further delocalization and improve the conductivity as well as mobility at higher temperature as compared to acetone solvent.

We also investigated the stability response of (a) PANI (b) PANI + IPA and (c) PANI + Acetone devices by measuring the electrical responses continuously for 16 h at 50 ± 5 °C under the laboratorical environments. We selected conductivity as well as mobility for stability analysis as these parameters are one of the fundamental parameters to define conducting polymer electrical response and can easily be measured. The conductivity was directly measured, while mobility was estimated from SCLC for each two-hour intervals. The degradation of normalized conductivity and mobility responses for are (a) PANI (b) PANI + IPA and (c) PANI + Acetone devices are shown in figure 8 respectively. It is observed from the figure that both these parameters are steadily and significantly degraded for each devices like many other reported conducting polymers \cite{32, 33}. The relatively fast decay of conductivity and mobility for PANI as compared to PANI + IPA and PANI + Acetone specifies that solvent also improves the stability of PANI, which required further detailed investigations. The main reason for the degradation of PANI is its sensitivity with both oxygen and moisture contents present in the environment, which can easily be limited by applying some protection through rigid glass or flexible poly (ethylene terephthalate) (PET) or poly(ethylene naphthalate) (PEN) type of encapsulation.

4. Conclusion

In conclusion, we investigated the effect of solvent IPA and acetone on the charge transport mechanism of PANI as a function of temperature. From SEM and XRD characterization, it is noted that both solvent improves the surface smoothness and negligible solvent traces were observed in final thin-film devices. It is also observe that PANI follows SCLC model to define their electrical properties and therefore the mobility from SCLC model were calculated and compared the conductivity and mobility of PANI with IPA and acetone as a function of temperature and found that relatively high boiling point solvents not necessarily improve the conductivity and
motility of PANI due to complex behaviour of solvent induced self-organization of molecular chains and residual traps reduction as a function of temperature.

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