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Effect of gravity condition on charge transport properties of polymer thin film deposited by centrifigual method

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Poly-N Epoxipropylcarbazole (PEPC) doped by anthracene (An) based diodes were fabricated by centrifugal deposition equipment at different gravity conditions: 1g, 123g, 277g and 1107 g (g = 9.81 m/sec). All devices followed three dimension variable range hopping mechanism and therefore different hopping parameters such as Mott characteristics temperature and hoping distance as a function of gravity conditions were estimated and discussed. Characteristics temperature and hoping distances are improved for the devices fabricated at higher gravity conditions and the device fabricated at 277g demonstrates most optimum charge transport response due to improvement in the orderness of molecular chains in polymer thin film.

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1. Introduction

Charge transport mechanism in semiconducting polymer is complicated and controversial. Still no any unanimously accepted charge transport model is available to optimize the electrical response for polymer electronic devices [1]. Like other charge transport models, variable range hopping (VRH) model is fruitfully practicable for disordered organic/polymer semiconductor devices even at room or above room temperature [2-4].

Different functional groups attached to the main molecular chain play vital role to define the electrical response for polymer. Functional group carbazole based polymers have attracted a great attention due to their excellent electron donating properties for efficient bulk heterojunction solar cell and hole transporting layer for polymer light emitting diode, polymer thin film transistor and many other electronic devices [5]. One of these polymers, poly-N-epoxypropylcarbazole (PEPC) have already reported in literature for successful fabrication of light emitting diode, thin film transistor, solar cell, and different type of sensors [6,7], but polymer material still facing lack of information [8,9].

Method used for the deposition of polymer thin film significantly impact on the device performances. Different deposition methods, such as vacuum thermal evaporation, chemical vapor deposition, organic molecular beam deposition, spin-coating deposition, centrifugal deposition, ink jet printing, screen printing and other deposition methods have been reported for many different polymer electronic devices [11]. Among these methods, centrifugal deposition method is a simple, novel, unique and emerging method for thin film deposition of organic/polymer material at different gravity conditions [6,8-10,12].

Therefore, in this study, the simple PEPC thin films were deposited by centrifugal deposition method with similar electrode materials and processing parameters except gravity conditions. The electrical responses of the devices were investigated as a function of temperature with the help of VRH model. By comparing the hopping transport parameters, the most optimum gravity condition for centrifugal thin film deposition was determine and discussed.

2- Experimental

The detailed information about the synthesis of PEPC (n = 4-6, weight 1000 amu) is described in [13]. The PEPC solution were made in toluene from the 25 wt.% PEPC doped by 10 wt. % An. Thin films of PEPC were grown at room temperature by using a centrifugal equipment at gravity conditions 1 *g*, 123 *g*, 277 *g* and 1107 *g*; where *g* is acceleration due to gravity (9.8 cm^2/V. sec).

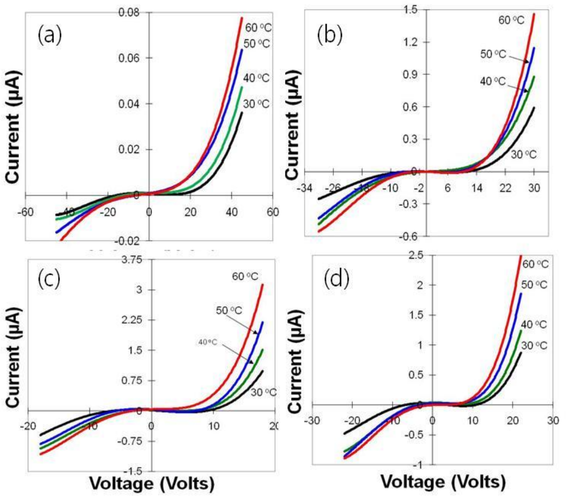

Fig. 1. Current-voltage characteristics of the device Ni/PEPC-An/Ga fabricated at different gravity conditions such as (a) 1g, (b) 123g, (c) 277g, and (d) 277 g, respectively.

Detailed information about the centrifugal equipment and processing method can be found in our already published results [6,9]. Here, reference sample was fabricated at 1*g* with processing time ranging from 20 to 24 hours. Simple visual inspection showed that the films grown at higher acceleration were relatively homogeneous compared to those deposited at lower gravity conditions.

3. Results

I-V characteristics of the PEPC based devices fabricated at 1g, 123g, 277 g and 1107 g as a function of temperature are shown in Fig. 1. In all these figures more or less similar *I-V* response is observed, except the differences in the scale of current. When gravity conditions for thin film deposition are increases then the current passing through the devices is also increases. But the device fabricated at 277 g shows the highest current rating.

Fig. 2a shows the Ln σ of PEPC thin films as a function inverse of temperature (T^{-1}). Generally, conductivity and temperature response for most amorphous semiconductor are correlated with Arrhenius type equation, can be expressed as

$$\sigma = \sigma_0 \; Exp\left[-\frac{E_a}{kT}\right] \qquad (1)$$

where E_a, σ_o and k are the activation energy, Arrhenius pre-factor and Boltzmann constant respectively. Using standard least square method weakly fitted (low value of coefficient of determination R^2) straight line, for Arrhenius response is observed for all devices.

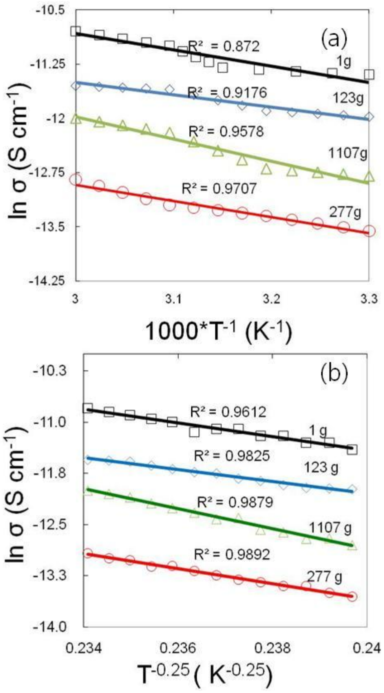

Fig. 2. The natural logarithmic dc conductivity (lnσ) as a function of (a) inverse temperature and (b) $T^{-0.25}$ for all devices fabricated at 1g, 123g, 277g, and 277g.

The nonlinear Arrhenius responses of all devices indicate that the band conduction type model is not adequate to explain the charge transport mechanism for devices fabricated at different gravity conditions.

Therefore to go into more detail, Mott hopping transport model was applied to investigate the effect of gravity conditions onto the charge transport mechanism for all devices. According to the Mott VRH model, temperature dependent conductivity (σ [T]) in amorphous polymer semiconductor materials may be written as [14]

$$\sigma(T) = \sigma_0 \; Exp\left[-\left(\frac{T_o}{T}\right)\right]^{\gamma} \qquad (2)$$

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Where T_o is the Mott characteristics temperature, σ_o is defined as the Mott pre-exponential factor.

Table 1. Variable range hopping parameters of Ni/PEPC-An/Ga devices fabricated at different gravity conditions.

Device Fabricated at	T_o	R (300 K)	R (330 K)
	K	m	m
1 g	7.04E+07	9.13E-08	8.95E-08
123 g	9.39E+07	8.89E-08	8.66E-08
277 g	1.37E+08	8.23E-08	7.94E-08
1107 g	1.28E+08	8.73E-08	8.49E-08

While γ, is the exponential term used to define the dimensionality (d) of the variable hopping transport mechanism as $\gamma = 1/(d+1)$. For d = 3, 2 and 1 dimension the typical value of γ is 0.25, 0.33 and 0.5 respectively. By plotting a graph between ln σ vs $T^{-0.25}$, nearly straight lines with relatively high coefficient of determination (average $R^2 \sim 0.98$ for all devices, while max $R^2 = 1$) were obtained for each device as shown in Fig. 2(b). It shows that all devices follow three dimension variable range hopping charge transport mechanism independent of gravity conditions. If we take the natural logarithm on both side of equation 1, then the following relationship is obtained

$$\ln\sigma = \ln\sigma_o - (T_o)^{\frac{1}{4}} \; (T)^{-\frac{1}{4}} \qquad (3)$$

Where Mott characteristics temperature, T_o was calculated for each device from the slope of the fitted straight line provided by equation 3. According to the Mott theory of VRH, the characteristics temperature (T_o) can be define as [14]

$$T_o = \frac{\lambda\alpha^3}{N(E_f)k} \qquad (4)$$

Where λ is a dimensionless constant (-18.1), α describe the spatial extent of localized wave function and $N(E_f)$ is the density of state at the Fermi level. By assuming $N(E_f) = 10^{19}$ cm^{-3} ev^{-1}, commonly reported for polymer semiconductor [15], it is possible to determine the hopping distance R from the Mott model as [14]

$$R = \left[\frac{9}{8\pi \alpha k T N(E_f)} \right]^{\frac{1}{4}} \tag{5}$$

By using α, calculated from equation (4), R is calculated for all devices at different gravity conditions and listed in Table 1. Other hopping parameters, such as hopping energy and hopping attempt frequency are not discuss here, because these parameters are simply derived from T_o and R, follow similar trend with T_o and R as discussed.

4. Discussion

In organic/polymer semiconductor, different atoms in a molecular chain are attached with covalent bond and provide strong intra-chain interaction. For inter-molecular chain interaction, each molecular chain is separated with other molecular chain by some amorphous region and inter-molecular charge transport takes place by variable range hopping mechanism. However, due to the weaker inter-molecular chain interaction, charges are localized on a chain and hops from one localized chain to another localized chain under the influence of applied electrical filed and temperature. Both inter and intra molecular interaction is greatly influenced by the gravity conditions during centrifugal deposition process and cause to establish different molecular structure for thin film deposition. Therefore, hopping transport parameters are directly depend on the gravity conditions during centrifugal thin film deposition process as clear from the Table 1.

When a PEPC solution in a centrifugal vessel on Ni substrate is angularly rotated at higher angular speed during centrifugal thin film deposition process, then many forces are acted on polymer chains in the solution at substrate. During angular rotation, the concentration of PEPC molecular chains is not same throughout the polymer solution at substrate. The variation of polymer chains concentration across the substrate in the presence of gravitational field crate a force called buoyancy force [12,16]. Like buoyancy many other forces such as hydrostatic, vibration, thermal, and coriolis force are also acting on the PEPC solution and make the centrifugal deposition process very complex to control. All these forces, especially buoyancy force at low gravity condition cause the random movement of PEPC chains as convection process with heat and mass transfer within polymer solution at substrate in the centrifugal vessel [17]. Such random movement of PEPC molecular chains during centrifugal thin film deposition process increases the disorderness and exposed by electrical response of polymer thin film. On the other hand, at higher gravity conditions the coriolis forces on molecular chains also become prominent and try to retard the bouncy driven convection in the polymer solution and improve the orderness of molecular chains in amorphous PEPC thin film [12,17]. Such improvement is reflected from the hopping parameters of the devices fabricated at high gravity conditions, listed in Table 1. Devices fabricated at higher gravity conditions show improved hopping parameters. As discuss above, the hopping of carriers from one polymer chain to the other molecular chain depends on the overlapping of chains and energy difference between chains. If the average molecular chain order is improved then average hopping process is also improved.

Mot characteristics temperature (T_o) can be defined as the effective energy barrier between localized molecular chains and it determine the degree of disorderness in the molecular chains. High value of T_o implies greater chain disorderness in the PEPC thin film devices and strong localization of carriers inside the molecular chains and results in the decreases of the conductivity. Therefore the characteristic temperature of the devices increases when the gravity condition (improved disorderness) is increases and the device fabricated at 277g shows the highest value of characteristics temperature.

Just like T_o, the R is another important parameter to evaluate the transport mechanism for polymer. Large value of R implies that molecular chains are far-away to each other and offer low coupling between them. From Table 1 it is observed that at room temperature (300 K), R is decreases for the devices fabricate at high gravity conditions due to improvement of the chains disorderness and quality of thin films with high inter-chain coupling. The device fabricated at 277g shows lowest R with highest inter-chain coupling.

Molecular chains in polymer thin film are randomly vibrated even at room temperature and such random movement creates defects in the polymer chains as twisting, folding, vibration and irregular rotation of the molecular chains inside polymer. At higher temperature, the molecular vibration significantly increases and it is experimentally observed that molecular chain defects specially twisting and folding of molecular chains are improved in polymer. Removals of chain defects in polymer cause to straighten the molecular chins and further decreases the overall hopping distance as reflected by value R at 330 K in Table 1.

For improved electrical response for device fabricated at 277g, different theories are reported, but still no any satisfactory answer is available. It is unanimously accepted that maximum convection suppression at a particular rotation rate during thin film deposition may cause to provide the best quality of thin film to optimize the electrical response at 277 g. Wilcox discussed different models name as flow transition model, thermal stability model and buoyancy-coriolis balance model, to explain the maximum suppression of convection process, detail information can be found in [17].

5. Conclusion

Charge transport mechanism of PEPC-An based devices fabricated by centrifugal method at different gravity conditions such as 1g, 123g, 277g and 1107 g were investigated and discussed. From electrical response, it is observed that all devices follow three dimension variable range hopping model for their charge transport mechanism. Different hopping parameters were estimated as a function of gravity conditions and it is observed that hopping parameters were improved at higher gravity condition and device fabricated at 277g shows the most optimum electrical response, owing to the improvement in the disorderness of the thin film.

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References

[1] J. Cornil, D. Beljonne, J. P. Calbert, J. L. Bredas, Adv. Mater. **13**, 1053 (2001).

[2] A. K. Himanshu, S. K. Bandyopadhayay, P. Sen, N. N. Mondal, A. Talpatra, G. S. Taki, T. P. Sinha, Radiat. Phys. Chem. **80**, 414 (2011).

[3] C. Basavaraja, N. R. Kim, E. A. Jo, D. S. Huh, J. Polym. Res. **17**, 861 (2010).

[4] K. R. Rajesh, C. S. Menon, J. Non. Crys. Sol. **351**, 2414 (2005).

[5] J. Lia, A. C. Grimsdale, Chem. Soc. Rev. **39**, 2399 (2010).

[6] M. M. Ahmed, Kh. S. Karimov, S. A. Moiz, IEEE Trans. Electron. Dev. **51**, 121 (2004).

[7] I. F. Perepich.k, D. D. Mysyk, N. I. Sokolov, Synth. Met. **101**, 9 (2001).

[8] S. A. Moiz, M. M. Ahmed, Kh. S. Karimov, F. Rehman, J.-H. Lee, Synth. Met. **159**, 1336 (2009).

[9] S. A. Moiz, M. M. Ahmed, K.h. S. Karimov, M. Mehmood, Thin Solid Films, **516**, 72 (2007).

[10] Kh. S. Karimov, I. Qazi, S. A. Moiz, I. Murtaza, Optoelectron Adv. Mater. – Rapid. Commun. **2**, 219 (2008).

[11] M. M. Ling, Z. Bao, Chem. Mater. **16**, 4824 (2004).

[12] W. R. Wilcox, L. L. Regel, W. A. Arnold, J. Cryst. Growth **187**, 543 (1998).

[13] Kh. M. Akhmedov, Kh. S. Karimov, I. M. Shcherbakova, Yu. N. Porshnev, M. I. Cherkashin, Russian Chem. Rev. **59**, 738 (1990).

[14] N. F. Mott, E. A. Davis, Electronic Processes in Non-crystalline Materials, Clarendon, Oxford, 1979.

[15] A. Raghunathan, P. K. Kahol, J. C. Ho, Phys. Rev. B. **58**, 955 (1998).

[16] P. V. Skudarnov, L. L. Regel, W. R. Wilcox, J. Cryst. Growth, **193**, 219 (1998).

[17] L. L. Regel, W. R. Wilcow, “Processing by Centrifugation,” Proceedings of the Fourth International Workshop on Materials Processing at High Gravity, May 29-June 2, 2000, Clarkson University, Potsdam, New York.

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