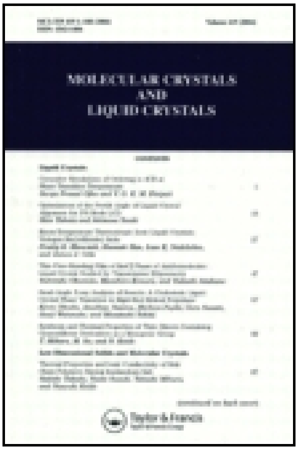

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Effect of Thermal Annealing on the Charge Carrier Mobility in a Polymer Electroluminescent Device

Tae-Woo Lee [a] , Yong-Min Kim [b] & Young Chul Kim [b]
[a] Samsung Advanced Institute of Technology, Giheung-gu, Yongin-si, Gyeonggi-do, Korea
[b] Materials Research Center for Information Display, College of Environment and Applied Chemistry, Kyung Hee University, Yongin-si, Gyeonggi-do, Korea

Version of record first published: 17 Oct 2011

To cite this article: Tae-Woo Lee, Yong-Min Kim & Young Chul Kim (2006): Effect of Thermal Annealing on the Charge Carrier Mobility in a Polymer Electroluminescent Device, Molecular Crystals and Liquid Crystals, 462:1, 241-248

To link to this article: http://dx.doi.org/10.1080/15421400601013387

Mol. Cryst. Liq. Cryst., Vol. 462, pp. 241–248, 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400601013387

Effect of Thermal Annealing on the Charge Carrier Mobility in a Polymer Electroluminescent Device

Tae-Woo Lee
Samsung Advanced Institute of Technology, Giheung-gu, Yongin-si, Gyeonggi-do, Korea

Yong-Min Kim
Young Chul Kim
Materials Research Center for Information Display, College of Environment and Applied Chemistry, Kyung Hee University, Yongin-si, Gyeonggi-do, Korea

Effect of thermal annealing on the time-of-flight charge carrier mobility of a polymer electroluminescent device was investigated. The average hole mobility of the device before annealing was $\sim 1\times 10^{-6}\,cm^2/V/s$*, while the thermally annealed device demonstrated both dispersive carrier transport characteristics and enhanced carrier mobility (*$\sim 3\times 10^{-6}\,cm^2/V/s$*). This is attributed to the increased interchain interactions achieved by thermal annealing. It was clarified that with the higher degree of interchain interactions the faster becomes the charge carrier mobility. We propose the thermal annealing method as a convenient and effective mean to improve the carrier mobility of the devices based on organic/polymeric semiconducting materials.*

Keywords: annealing; charge carrier mobility; light-emitting diodes; time-of-flight technique

INTRODUCTION

Polymeric semiconductors offer an attractive alternative to the conventional inorganic semiconductors for electronic and optoelectronic applications due to their compatibility with flexible substrates as well

This work was supported by grant No. R01-2005-000-10852-0 from the Basic Research Program of the Korea Science & Engineering Foundation.

Address correspondence to Young Chul Kim, College of Environment and Applied Chemistry, Kyung Hee University, Yongin-si, Gyeonggi-do 449-701, Korea. E-mail: kimyc@khu.ac.kr

as high luminescence efficiency and low production cost. The first report on the light-emitting diode (LED) consisting of a conjugated polymer, poly(*p*-phenylene vinylene) [1], triggered a lot of researches on photonic, electronic, and optoelectronic devices based on the polymeric semi-conducting materials, such as field-effect transistors [2], lasers [3], and LEDs [1]. Fast and balanced transport of charge carriers is required for the fabrication of high efficiency polymer LEDs and the realization of electrically-driven polymer lasers. In addition, achievement of high carrier mobility has a key to the commercialization of organic transistors.

The photophysical and electrical behaviors of conjugated polymer films depend on the chain aggregation and morphology [4]. Thus, the photoluminescent (PL) and electroluminescent (EL) characteristics of solvent-cast polymer films can be controlled by the type of solvent [5], polymer concentration in the solution [5], spin-speed [4], thermal annealing [6–9], and etc, which change the degree of interchain interaction. We have reported the thermal annealing effect on the luminescent efficiency of the LED based on poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) [6], which has been followed by the subsequent reports by other groups [7–9]. It has also been suggested that higher degrees of interchain interaction facilitates charge transport [4], but the result has not yet been demonstrated quantitatively. In this work, we report the effect of thermal annealing on the charge carrier mobility in polymer LEDs, which was investigated by the photo-induced time-of-flight (TOF) technique [10].

EXPERIMENTAL

MEH-PPV dissolved in dichloroethane was spin-cast on an indium tin oxide (ITO)-coated glass substrate to give a 230 nm-thick film: We tried to obtain the thin film in order to perform the TOF experiments under actual operation conditions of polymer LEDs. We observed a non-dispersive transport phenomenon even in this thin film when we excited the specimen with a low energy below 20 μJ/cm^2/pulse. The as-cast MEH-PPV film was dried under vacuum of $\sim 10^{-6}$ torr for 2 hrs and Al was deposited as the cathode on the top of the film by thermal evaporation (also under $\sim 10^{-6}$ torr vacuum). The device was thermally annealed at 150°C in a vacuum oven for 1 hr. A pulsed nitrogen laser (GL-3000, Photon Technology, 337.1 nm, 800 ps) generates a sheet of carriers that then drift across the device connected to a power supply. The transient photocurrent was measured by recording the voltage drop across a resistor connected to the metal electrode and to the ground. A digital storage oscilloscope (Infinium 54810A, Hewlett Packard, 500 MHz) was used to measure the voltage change with time. The transit time for the arrival of carriers, t_T, is related to the carrier mobility μ via the relation $\mu = d/t_T E$, where d is the film thickness and E the external bias field. The profiles were collected at a low bias field between 1.0 and 2.1 V to avoid electron injection. All measurements were performed at room temperature.

RESULTS AND DISCUSSION

Figure 1 shows the TOF photocurrent profile obtained while applying 1.5 V to the EL device before thermal annealing. The initial current spike is followed by a constant current plateau. This corresponds to non-dispersive hole transport, which has been observed in the previous studies [11,12]. Carrier transit time, t_T, is readily determined from the intersection point of the two asymptotes on the double-logarithmic current-time plot as shown in the inset of Figure 1. The average hole mobility of the device before annealing was $\sim 1 \times 10^{-6}\,\mathrm{cm^2/V/s}$, which is close to the previously reported values [12]. When we thermally annealed the device, however, the TOF profile and the mobility were obviously changed as Figure 2 demonstrates: the charge transport

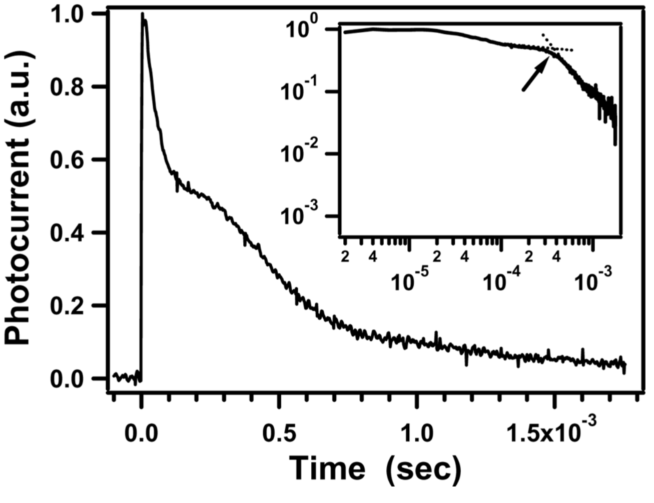

FIGURE 1 The TOF transient photocurrent profile for the unannealed MEH-PPV device. The profile was measured at a bias field of $6.5 \times 10^{-4}\,\mathrm{V/cm}$ and plotted in both linear and double-logarithmic (inset) scales. The transit time was determined from the intersection of the asymptotes to the double-logarithmic transient photocurrent plots.

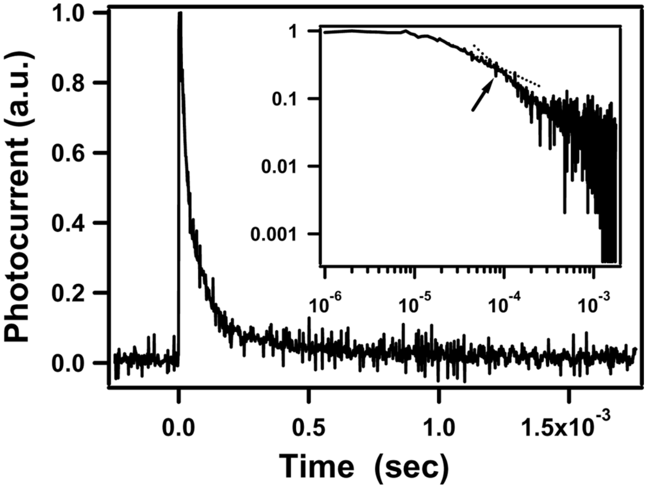

FIGURE 2 The TOF transient photocurrent profile for the MEH-PPV device annealed at 150°C. The profile was measured at a bias field of 6.5×10^{-4} V/cm and plotted in both linear and double-logarithmic (inset) scales.

became dispersive and the charge carrier mobility increased up to $\sim 3 \times 10^{-6}$ (cm^2/V/s). We can clearly observe the transition from non-dispersive to dispersive charge transport upon annealing. This kind of transition in the charge transport has been found at low temperature [12,13]. It has also been known that hopping within an intrinsic distribution of hopping states gives rise to dispersive transport even in the absence of traps. Recently, Blom *et al.* [14] reported that the dispersive nature of hole transport comes mainly from structural disorder, rather than from energetic disorder. Therefore, we can consider that the thermal annealing of conjugated polymers broadens the transit time distribution of the carriers by inducing a kind of structural disorder: since the thermal annealing obviously favors π-π stacking in conjugated chains, we could infer that the structural disorder may result from the chain stacking. Besides thermal annealing, the π-π stacking can be more facilitated by spin-casting conjugated polymer films with an aromatic solvent such as cholorobenzene, xylene and etc. Therefore, the use of non-aromatic solvent and the solvent-drying below the glass transition temperature (T_g: 65°C for MEH-PPV) might lead to non-dispersive charge transport.

Figure 3 shows the TOF charge carrier mobilities of the device before and after the thermal annealing. The charge carrier mobility tends to gradually decrease when measured at low bias fields as

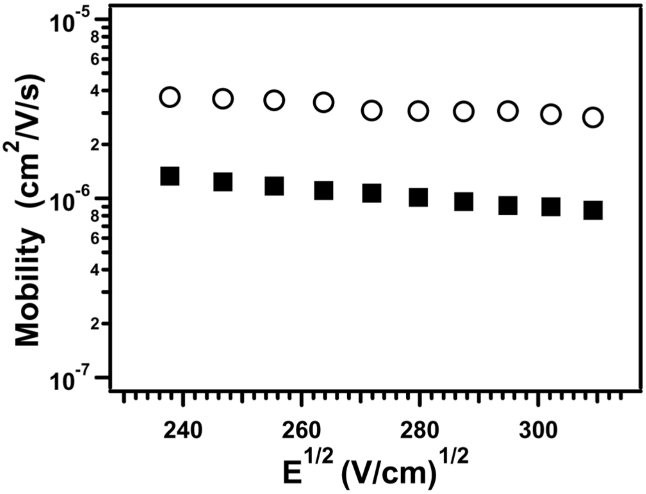

FIGURE 3 Bias field dependence of the hole mobility in the MEH-PPV device at room temperature before and after the thermal annealing at 150°C.

observed by other researchers [11,15,16]. Bässler has interpreted this as the hopping of charge carriers in the simultaneous presence of diagonal (energetic) and off-diagonal (positional) disorders based on Monte Carlo simulations [15]: the hopping transport model accounts for off-diagonal disorder with variations of intersite distances in addition to diagonal disorder in the transport manifold. A large off-diagonal disorder results in a negative field dependence of the mobility at low fields.

Our concern also lies in the correlation between the charge carrier mobility and the EL efficiency of the thermally annealed devices. Although the increased chain interactions in the annealed films usually lower the PL quantum yield, the post-deposition annealed device with Al cathode [6] and the pre-deposition annealed device with a low work function metal (e.g. Mg, Ca) [7,9] gave a lower turn-on voltage [6,7,9], higher light output [6,7], and sometimes higher EL quantum yield [7]. The Mg device of the Schwartz' group [7] based on the single-layer film (or aggregated-morphology film) thermally annealed prior to the cathode deposition showed a higher EL quantum efficiency, while the Ca device of the Yang's group [9] based on the single-layer film annealed prior to the cathode deposition gave a lower EL efficiency. This discrepancy is controversial. However, when the both groups tried bi- or tri-layer devices composed of annealed and unannealed films, the EL efficiency was obviously increased by annealing.

This means that thermal annealing helps the emitting materials to transport both electrons and holes more efficiently.

In addition, it has been reported that the interchain interaction increased by changing the solvent (or by increasing its aromaticity), the solution viscosity, and the spinning speed leads to a low turn-on voltage and a higher quantum yield [5]. It has also been suggested that thermal annealing of the films or the devices will facilitate carrier injection and transport [4,6,7]. This TOF measurement makes it clearer that the increased π-π overlap by thermal annealing facilitates charge carrier transport.

In the case of the post-deposition annealed device with Al cathode, which is a rather high workfunction metal, both the electron injection and the EL efficiency were largely enhanced (also see Figure 4), suggesting the enhanced interfacial characteristics by the formation of an interfacial layer comprising Al-O-C bonds [6]. Therefore, the high EL efficiency of the post-deposition annealed device is considered to be a combinatory effect of both the enhanced electron injection and carrier mobility. Although we measured only the hole mobility, one underlying question is whether the electron mobility in MEH-PPV after the post-deposition annealing will be also enhanced or not. When our results are combined with those of the tri-layer device of chlorobenzene (CB)-cast layer/tetrahydrofuran-cast layer/CB-cast layer

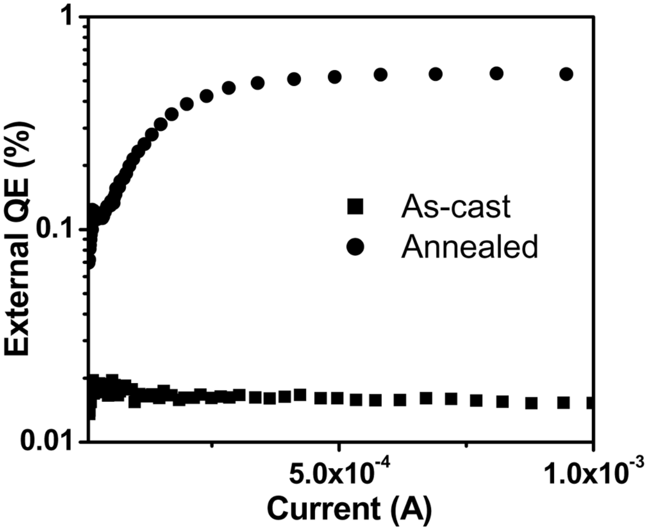

FIGURE 4 External quantum efficiency of the MEH-PPV device measured as a function of current before and after the thermal annealing at 150°C.

tried by Schwartz' group [7], it becomes clearer that the electron mobility is also enhanced. As a result, although MEH-PPV is a good transporter of both holes and electrons as reported by Bozano *et al.* [17], both carrier transport will be even more promoted after thermal annealing.

CONCLUDING REMARKS

The effect of thermal annealing on the time-of-flight charge carrier mobility of the EL device based on a conjugated polymer was investigated under the actual operating condition of the device. Thermal annealing induces higher interchain interactions so that the annealed device showed the dispersive carrier transport characteristics and higher mobility. This work demonstrates that with the higher degree of interchain interactions, the faster becomes the charge transport mobility. Therefore, we can conclude that the thermal annealing above the materials' T_g provides a convenient and effective mean to improve the carrier mobilities of the LEDs, electrically-driven lasers, and transistors made of polymeric semiconducting materials.

REFERENCES

[1] Burroughes, J. H., Bradley, D. D. C., Brown, A. R., Marks, R. N., Mackay, K., Friend, R. H., Burn, P. L., & Holmes, A. B. (1990). *Nature (London)*, *347*, 539.

[2] Sirringhaus, H., Tessler, N., & Friend, R. H. (1998). *Science*, *280*, 1741.

[3] (a) McGee, M. D. & Heeger, A. J. (2001). *Adv. Mater.*, *12* 1655.
  (b) Kim, Y. C., Lee, T.-W., Park, O. O., Kim, C. Y., & Cho, H. N. (2001). *Adv. Mater.*, *13*, 646.

[4] Nguyen, T.-Q., Martini, I. B., Liu, J., & Schwartz, B. J. (2000). *J. Phys. Chem. B*, *104*, 237.

[5] (a) Shi, Y., Liu, J., & Yang, Y. (2000). *J. Appl. Phys.*, *87*, 4254.
  (b) Liu, J., Shi, Y., Ma, L., & Yang, Y. (2000). *J. Phys. Chem. B*, *88*, 605.

[6] (a) Lee, T.-W. & Park, O. O. (2000). *Adv. Mater.*, *12*, 801
  (b) Lee, T.-W. & Park, O. O. (2000). *Appl. Phys. Lett.*, *77*, 3334.
  (c) Lee, T.-W., Park, O. O., Do, L.-M., & Zyung, T. (2001). *Synth. Met.*, *117*, 249.

[7] Nguyen, T.-Q., Kwong, R. C., Thompson, M. E., & Schwartz, B. J. (2000). *Appl. Phys. Lett.*, *76*, 2454.

[8] Jung, G. Y., Yates, A., Samuel, I. D. W., & Petty, M. C. (2001). *Mat. Sci. Eng.*, *14*, 1.

[9] Liu, J., Guo, F.-T., & Yang, Y. (2002). *J. Appl. Phys.*, *91*, 1595.

[10] Borsenberger, P. M. & Weiss, D. S. (1998). *Organic Photoreceptors for Electrophotography*. Marcel Dekker: New York.

[11] (a) Redecker, M., Bradley, D. D. C., Inbasakeran, M., & Woo, E. P. (1998). *Appl. Phys. Lett.*, *73*, 1565.
  (b) Redecker, M., Bradley, D. D. C., Inbasakeran, M., & Woo, E. P. (1999). *Appl. Phys. Lett.*. *74*, 1400.

[12] Inigo, A. R., Tan, C. H., Fann, W., Huang, Y.-S., Perng, G.-Y., & Chen, S.-A. (2001). *Adv. Mater.*, *13*, 504.

[13] Borsenberger, P. M., Pautmeier, L. T., & Bässler, H. (1992). *Phys. Rev. B*, *46*, 12145.

[14] Blom, P. W. M. & Vissenberg, M. C. J. M. (1998). *Phys. Rev. Lett.*, *80*, 3819.

[15] Bassler, M. (1993). *Phys. Status Solidi B*, *175*, 15.

[16] Hertel, D., Bässler, H., Scherf, U., & Hörhold, H. H. (1999). *J. Chem. Phys.*, *110*, 9214.

[17] Bozano, L. S., Carter, A., Scott, J. C., Malliaras, G. G., & Brock, P. J. (1999). *Appl. Phys. Lett.*, *74*, 1132.