

Thermally Stimulated Luminescence In Photoconducting Doubly-Doped Polymers

Andrey K. Kadashchuk[1] and David S. Weiss[2]
[1)] Institute of Physics, Natl. Academy of Sci., Prospect Nauki 46, 03028, Kiev
[2)] Heidelberg Digital L.L.C., Rochester, New York

Abstract

We have measured thermally stimulated luminescence (TSL) in tri-p-tolylamine doped poly(styrene) containing various concentrations of different extrinsic shallow traps. The evolution of the distribution of localized states in these doubly-doped polymers was studied with increasing trap concentration and trap depth. We show that the observed trends in the TSL can be reasonably well understood, in terms of the Gaussian disorder model, as thermal release of charge carriers from the tail states of the density-of-states distribution. Our approach is based on analysis of the fractional TSL data and allows extraction of a parameter characterizing the energetic disorder in disordered organic solids. The effect of shallow extrinsic trapping on TSL properties, due to molecules with lower ionization potential, can be reasonably interpreted in terms of the effective energetic disorder and the TSL results are in good agreement with those obtained earlier by charge transport studies.

Introduction

Investigation of intrinsic energetic disorder, and extrinsic trapping processes, are an important task for better understanding of both transport and injection phenomena in materials promising for OLED applications. In addition to a fundamental interest in charge transport models, knowledge of the trap distributions can provide guidance for materials selection and preparation.

Molecularly doped polymers (MDPs) are of great interest due to their current application as charge transport layers in organic electrophotographic photoreceptors[1] and electro-luminescent devices,[2,3] etc. Most recent studies of charge transport in MDPs have been described within the framework of the Gaussian disorder model[4] of Bässler and coworkers. The model is premised on the argument that charge carrier transport occurs by hopping through a manifold of localized states with a Gaussian density-of-states (DOS) distribution characterized by a width σ. A fundamental assumption of the model is that the disordered systems are trap-free, i.e. charge transport is controlled only by the intrinsic localized state distribution caused by disorder effects. Trapping is due to the presence of extrinsic localized states that differ from the majority of hopping states in that they require a larger energy input to release the charge carriers back to the intrinsic DOS.

One of the most important problems of the disorder formalism is to describe carrier transport in the presence of extrinsic traps. This has led to the recent interest in trapping effects in MDPs.[5-7] In these materials, traps were deliberately introduced by so called double-doping. Two charge transport materials are dissolved together in a polymer matrix, where the transport energy of one is offset from the other. Thus, hole transport would be affected by trapping on charge transport molecules having a lower ionization potential. Recently Wolf et. al.[5] and Borsenberger et. al.[6] extended the disorder model to include the effect of extrinsic trapping. The results of computer simulations and photocurrent transient measurements show that the presence of a distribution of shallow traps, offset from the intrinsic DOS by energy E_t, does not change the basic phenomenology of transport. Trapping effects can be quantitatively accounted for by replacement of σ with an effective (broader) width σ_{eff} according to:

$$(\sigma_{eff}/\sigma)^2 = 1 + (3\kappa T/2\sigma)^2 (E_t /\kappa T + \ln c), \qquad (1)$$

where c is the trap concentration. An important conclusion is that the trap-free and shallow trap-controlled transport regimes should be qualitatively indistinguishable.

The thermally stimulated luminescence (TSL) method and its modification, fractional TSL, are well suited for the determination of the energetic depth and distribution of traps. Recently, low-temperature TSL was applied in the evaluation of the energetic disorder parameter in polymers with carbazole pendant groups,[8] σ-conjugated polysilylenes,[9,10] certain π-conjugated polymers,[11] as well as some MDPs.[12,13] Our approach is based on the assumption that at very low temperatures the lowest energy portion of an energetically disordered manifold of localized states may manifest itself as trapping centers for charge carriers. Therefore, by analyzing the TSL trap distribution function, one may estimate the shape of the deepest part of the DOS distribution and, consequently, the parameter of the energetic disorder, σ.

The present study is focused on the TSL of doubly-doped polymers, with increasing shallow-trap concentration and trap depth, to provide a detailed insight into the evolution of the distribution of localized states and the detrapping process. The doubly-doped polymer systems

studied are essentially the same as used recently by Borsenberger et. al. for charge transport measurements[6]: tri-p-tolylamine (TTA) doped poly(styrene) (PS) contain-ing various concentrations of di-p-tolyl-p-anisylamine (DTA), di-p-anisyl-p-tolylamine (DAT) or tri-p-anisyla-mine (TAA). Trap depths (the difference in ionization potential from TTA) of DTA, DAT, and TAA are 0.08, 0.15, and 0.22 eV.[6]

Experimental

The charge transporting materials (TTA, DTA, DAT, and TAA) were supplied by the Eastman Kodak Company. MDP films (thickness about 10 μm) were prepared by dissolving the appropriate ratios of these compounds and PS in dichloromethane, then casting the resulting solutions on a stainless steel substrate. The films were dried in vacuo for several hours. The concentration of the DTA, DAT or TAA ranged from a few hundredths up to several weight percent with respect to TTA. The total concentration of charge transporting molecules in all samples was 40% with respect to PS.

TSL measurements were carried out over a wide temperature range (4.2 to 350 K). TSL measurements after UV light excitation were performed with two different methodologies: uniform heating at a rate $\beta = 0.15$ K/s, and fractional heating. The latter procedure allows the determination of trap depth when different groups of traps are not well separated in energy or are continuously distributed. The fractional TSL technique, being an extension of the initial rise method, is based on cycling the sample with a large number of small temperature oscillations superimposed on a constant heating ramp. The main outcome of the fractional TSL is the temperature dependence of the mean activation energy, $\langle E \rangle(T)$.[8-14] The experimental details of and the data processing procedures have been described elsewhere.[9,12-14]

Results and Discussion

A typical TSL curve, TTA(40%) doped PS [TTA:PS], is shown in Figure 1. As can be seen, the TSL induced by UV exposure at 4.2 K is observed only in the low-temperature range. This indicates the presence of a large concentration of relatively shallow localized states capable of charge carrier capturing at this temperature. A quasi-continuous trap distribution has been found in this system.[12,13] The mean activation energies, <E>, as revealed by the fractional TSL, linearly increase with temperature (Fig.1, inset) according to the following empirical formula (in eV)

$$\langle E \rangle(T) = 0.0032T - 0.08. \quad (2)$$

In our earlier work,[12,13] we interpreted the low-temperature TSL of trap-free MDPs in terms of the thermal release of charge carriers from intrinsic tail states of the DOS. Since TSL measurements are normally performed after some dwell time, the initial energy distribution of localized carriers is formed after low-temperature (downward hopping) relaxation of photo-generated carriers within the DOS. This approach, based on the Gaussian disorder model, provides a reasonable understanding of all observed trends in the TSL. Analysis of the TSL peak of neat MDPs (see [12-13] for details) yields a width for the density of states profile for localized charge carriers which agrees reasonably well with the MDPs energetic parameter determined in the usual manner.

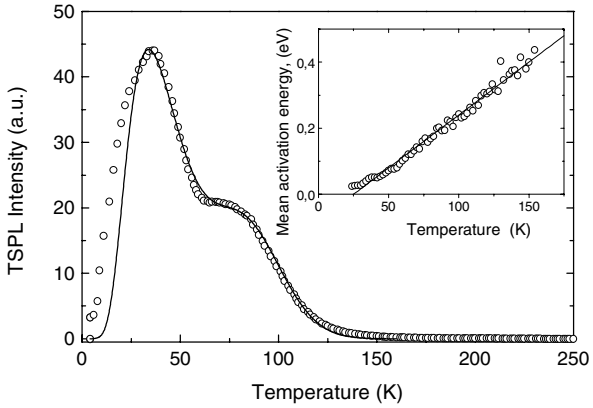

Figure 1. Experimental (circles) and theoretical (solid line) TSL glow curves of TTA(40%):PS. The inset shows the temperature dependence of <E>

More recently Arkhipov et. al.,[15] carried out the theoretical analysis of TSL in disordered organic materials using the concept of a thermally stimulated carrier random walk within a positionally and energetically random system of hopping sites. The analytical model describes most of the basic features of the TSL and permits calculation of the DOS distribution from the TSL data (for details see [15]). Figure 1 shows a comparison of the experimental TSL data of TTA:PS (circles) with the theoretical results (solid line).[15] It is worth noting that the model has verified that the energy distribution of trapped carriers must be an exact replica of the deeper portion of the DOS distribution. Also, the high-temperature tail of a TSL curve becomes a straight line when plotted on a log I *vs* T^2 scale (or log I *vs* E^2 after converting the temperature scale to a trap energy scale using the empirical calibration (Eq. 2)) with a slope that is a measure of the DOS width.

The results of Gaussian analysis of the high-temperature wing of the TSL peak of TTA:PS (Curve 1 in Figure 2) is consistent with the above model. The width of the distribution estimated from the slope is 0.074 eV. This agrees reasonably well with the width of the DOS, σ = 0.083 eV,[5,6] obtained from charge transport measurements. (It should be noted that, for simplicity sake, the concept of transport energy below the center of the DOS has been neglected, so the value obtained will be a slight under-estimate.) As was shown earlier,[12,13] the high-temperature part of TSL (which we refer to as the 'main TSL peak') is of major interest here since only the deepest portion of the

DOS governs charge carrier transport.[4-6] It was found[12,13] that the main TSL peak of TTA:PS can be readily separated with the additional exposure of a sample to IR-irradiation at 4.2 K following the conventional UV excitation (as can be seen by Curve 1 in Fig. 3). The effect was explained[9,12,13] in terms of acceleration of the energetic relaxation of photogenerated carriers within the Gaussian-shaped DOS.

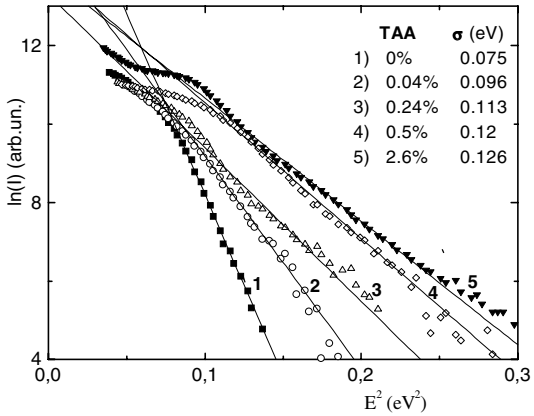

Figure 2. Gaussian analysis of the high-energy wings of TSL peaks of TTA:PS containing different concentration of TAA (E_t=0.22 eV).

This interpretation of the TSL data also presumes a linear relationship between the activation energy at the TSL peak maximum, $\langle E_m \rangle$, and the degree of energetic disorder. Such behavior has been observed[12] and it seems not to depend on type of polymer. A rather simple method was proposed for evaluation of the σ-value from the experimentally accessible value of $\langle E_m \rangle$: [9,10,12,13]

$$\sigma' = \langle E_m \rangle \left[(3\ln\ln(t/t_0))^{1/2}-1\right]^{-1} . \quad (3)$$

According to Eq. (3) one obtains σ' = 0.075 eV for the TTA:PS system.

Let us consider the trap-containing MDP systems. A good way to investigate the trap-controlled process of charge transport is provided by doubly-doping experiments, where a small amount of the more easily ionized molecules will act as a hole trap. As it was stated above, charge transport in doubly-doped MDPs as TTA:PS containing DTA, DAT, or TAA has been thoroughly studied by Borsenberger et. al.[6] and interpreted in terms of the effective disorder concept. Figure 3 summarizes the results of TSL measurements of TTA:PS containing various concentration of the above mentioned traps: DTA, DAT and TAA (Fig. 3(a), 3(b) and 3(c), respectively). All TSL glow curves in Fig. 3 were obtained under the same conditions (additional IR-irradiation for 30 min.). As one can see, the presence of even a small concentration of traps exerts a rather considerable effect on the TSL. The main TSL peak gradually shifts towards higher temperatures with increasing trap concentration.

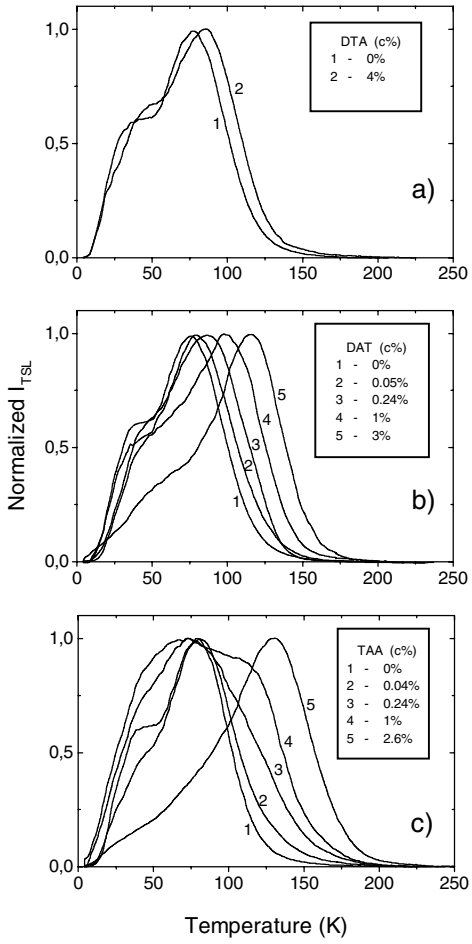

Figure 3. TSL glow curves of TTA:PS containing various concentration of the DTA (a), DAT (b) and TAA (c). Trap depths are 0.08, 0.15, and 0.22, respectively.

Another characteristic is that the effect of traps clearly depends on trap depth; i.e. the TSL shift becomes progressively more pronounced when DAT and TAA traps are used instead of DTA. This is in accord with a notion that the addition of traps has widened the DOS and agrees with results of charge transport measurements in these MDPs.[6] The lowest trap concentration level that affects the TSL glow curve also depends on the trap depth. With DAT and TAA, TSL changes were observed at c = 0.05%, while a DTA effect was seen only at c ≥ 1%.

It should be noted that the dependence of <E> on temperature (as measured by the fractional TSL technique) for all studied MDPs coincided well with that given by Eq. (2). The effect of the most shallow trap, DTA (E_t = 0.08 eV), on the TSL is relatively small, even at trap concentrations of 4%, although some shift of the high-temperature TSL peak towards higher temperatures is observed, Fig. 3(a). The activation energy at the TSL peak maximum increases from $\langle E_m \rangle$ = 0.17 eV (c = 0%) to 0.192 eV (c = 4%) which indicates an increase in the effective

energetic disorder from 0.075 to 0.085 eV according to Eq. (3).

A more pronounced effect was found for the DAT trap (E_t = 0.15 eV) (Fig. 3(b)). The activation energy at the maximum of the high-temperature TSL peaks is 0.17, 0.2, 0.215, 0.25 eV, for DAT concentrations c = 0%, 0.24%, 1%, 3%, respectively. These correspond to σ'-values of 0.075, 0.088, 0.095, and 0.11 eV as estimated by Eq. (3). These values agree reasonably with the σ_{eff} parameters: 0.083, 0.095, 0.101, and 0.107 eV obtained from charge transport measurements.[6] We stress that the characteristic high-temperature shift of the main TSL peak with increasing trap concentration, without the formation of new maxima, is most likely indicative of an increase in the σ_{eff}. Thus, the general picture of the TSL behavior of TTA:PS containing various concentrations of DAT is qualitatively undistinguished from that system without added traps.

The deeper TAA trap (E_t = 0.22 eV) has the strongest effect on the TSL (Fig. 3(b)). The high-temperature wing of the TSL exhibits a considerable shift towards higher temperatures with increasing TAA concentration demonstrating the appearance of deeper tail states. Gaussian analysis of the high-temperature wings of the TSL peaks of TTA:PS containing different concentrations of TAA is presented in Fig. 2. This data clearly demonstrates the broadening of the localized states distribution with increasing TAA concentration. From the slopes of the lines the widths of the distributions are estimated to range from 0.074 to 0.126 eV (see Fig. 2) for TAA trap concentrations increasing from 0 to 2.6%. The values obtained are in accord with the effective disorder parameters obtained from transport measurements[5,6]

It should be noted that among other things the present study provides a straightforward experimental test to distinguish between the disorder and polaron models.[1,16] According to the disorder model the distribution of trapped carriers is expected to gradually shift with increasing trap concentration towards deeper energy, reflecting a smooth increase in the width of the DOS. By contrast, if the polaron model applies, then small concentrations of the low-energy sites act as traps, leading to an immediate increase in activation energy. From the results presented it follows that the latter model clearly fails to explain the observed TSL behaviors of these doubly-doped MDPs. The TSL results are consistent with the disorder formalism.

Conclusions

Changes in the distributions of localized states in doubly-doped polymers with increasing trap concentration and trap depth was studied with the low-temperature TSL technique. The results obtained provide strong support for the hypothesis that the introduction of shallow "impurity" traps in MDPs leads to an effective increase in the energetic disorder. The resulting TSL peak reflects the superimposition of the disorder and trapping effects. Finally, TSL might be a suitable method for characterizing energetic disorder and extrinsic trapping in organic disordered materials of technological relevance. TSL could be a useful optical testing tool at the stage of materials selection and preparation.

References

1. P. M. Borsenberger and D. S. Weiss, Organic Photoreceptors for Xerography, Marcel Dekker, NY, 1998, pg. 768.
2. H. Antoniadis, B. R. Hsieh, M. A. Abkowitz, M. Stolka, Appl. Phys. Lett., **62**, 1367 (1993).
3. J. Pommerehne, H. Vestweber, W. Guss, R. F. Mahrt, H. Bässler, M. Porsch, J. Daub, Adv. Mat., **7**, 551 (1995).
4. H. Bässler, Phys. Status Solidi, B **175**, 15 (1993).
5. U. Wolf, H. Bässler, P.M. Borsenberger, W.T. Gruenbaum, Chem. Phys., **222**, 259 (1997).
6. P. M. Borsenberger, W. T Gruenbaum, U. Wolf, H Bässler, Chem. Phys., **234**, 277 (1998).
7. P. M. Borsenberger, E. H. Magin, S. A. Visser, Jpn. J. Appl. Phys., **37**, 1945 (1998).
8. A. Kadashchuk, N. Ostapenko, N. Lukashenko, Adv. Mater. Opt. Electr., **7**, 99 (1997).
9. A. Kadashchuk, N. Ostapenko, V. Zaika, S. Nešpùrek, Chem. Phys., **234**, 285 (1998).
10. S. Nešpùrek, A. Kadashchuk, N.Ostapenko, V. Zaika, Mol. Cryst. Liq. Cryst., **324**, 95 (1998).
11. A. Kadashchuk, Y. Skryshevskii, A. Vakhnin, N.Ostapenko, E. V. Emelianova, V. I. Arkhipov, H. Bässler, Phys. Rev., (submitted).
12. A. Kadashchuk, N. Ostapenko, V. Zaika, P.M. Borsenberger, J. Imaging Sci. Technol., **43**, 213 (1999).
13. A. Kadashchuk, D.S. Weiss, P.M. Borsenberger, N. Ostapenko, V. Zaika, Chem. Phys., **247**, 307 (1999).
14. I. A. Tale, Phys. Status Solidi, A **66**, 65 (1981).
15. V. I. Arkhipov, E. V. Emelianova, H. Bässler, A. Kadashchuk, Phys. Rev., (submitted).
16. L. B. Schein, Phil. Mag., B, 65, 109 (1992).

Biography

Dr. Kadashchuk is a Senior Researcher in the Institute of Physics of the Natl. Acad. of Sci. of Ukraine. He received a B.Sc. in physics from Kiev State University in 1984, and the Ph.D. degree from the Institute of Physics of the Ukrainian Acad. of Sci. in 1989. His research fields of specialization are spectroscopy, electronic processes in organic polymers and crystals, charge-carrier transport, trapping and photo-generation in organic solids. His current interests are principally directed to low-temperature thermoluminescence in disordered polymers as optoelec-tronic pi-conjugated polymers, polysilylenes, molecularly doped and pendant group polymers; low-temperature spectroscopy of polymers. He has published about 50 scientific articles.