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Organic Electronics 5 (2004) 53–58

Organic Electronics

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Analysis of deep traps in 4,4′-bis(4-dimethylaminostyryl benzene) based light emitting diode devices

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Received 9 January 2004; accepted 18 February 2004
Available online 7 March 2004

Abstract

Charge based deep level transient spectroscopy (Q-DLTS), a modified version of the conventional DLTS technique, has been used to characterize light emitting diodes made with 4,4′-bis(4-dimethylaminostryryl benzene) (DMASB), a poly(*p*-phenylene vinylene) (PPV) derivative containing amine groups. Analysis of the spectra obtained in ITO-DMASB-MgAg devices with different bias and temperature conditions has established that two types of traps exist within the band gap of the organic material. Traps of type I with a mean activation energy of ~0.38 eV and a capture cross section of the order of 10^{-17} cm^2 are identified as acceptor-like hole traps. These traps are believed to be distributed with a large deviation. Traps of type II have an activation energy of ~0.50 eV and a capture cross section of the order of 10^{-19} cm^2. They are assigned to donor-like electron traps. Comparing with the results obtained in PPV, we suggest that type I traps are related to the presence of the amine groups in the structure of the organic material.

Keywords: Deep level transient spectroscopy; Organic light emitting diodes; Traps

1. Introduction

In organic light emitting diodes (OLEDs), the charge injection at the electrodes and the carrier transport inside the active layer are of prime importance for the efficiency of the devices. These processes depend greatly on the electronic structure of the emitting material and it appears clearly that the energetic distribution of trap states inside the band gap influences strongly the electrical characteristics of the devices [1]. Knowledge of trap parameters in organic materials is therefore essential to determine the performance of devices. To investigate the trapping process, several spectroscopic methods are available such as current–voltage characteristics [2], impedance spectroscopy [3], and thermally stimulated currents [4]. Deep traps in semiconductors are usually studied by the

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doi:10.1016/j.orgel.2004.02.002

deep level transient spectroscopy (DLTS) [5]. In organic materials, because of the low mobility of the charge carriers, the relaxation time is high and from the practical point of view, highly resolved DLTS characteristics were difficult to obtain [6–8].

In this work, we have applied a modified DLTS technique to study the trap parameters in 4,4′-bis(4-dimethylaminostryryl benzene) (DMASB), a poly(*p*-phenylene vinylene) (PPV) derivative containing amine groups, which has shown promising characteristics for use in OLEDs. The technique used here is the charge based deep level transient spectroscopy (Q-DLTS) which differs from the conventional DLTS in that the charge is measured instead of the capacitance. We show that the trap parameters in DMASB can be determined with accuracy and the method can be applied to other organic materials in order to understand the trapping mechanism in relation with their electronic structure.

2. Experimental

ITO-DMASB-MgAg devices were fabricated as previously described [9]. The thickness of the organic layer was about 100 nm as measured by an Alphastep profilometer. *I–V* and Q-DLTS measurements were carried out using an automated system ASMEC-02, supplied by InOmTech Inc. The *I–V* measurements were performed in vacuum and at room temperature. Q-DLTS measurements were performed in the 100–315 K temperature range. The reproducibility of the measurements was ensured using a measurement protocol detailed elsewhere [10]. Details concerning the Q-DLTS theory can be found in the literature [11]. The technique can be summarized as follows. A Q-DLTS spectrum is obtained at a given temperature T in a two step cycle. Firstly, a voltage pulse ΔV is applied to the device for a duration τ_c (charging time). In some cases, an offset applied voltage V_0 can also be used. During this time, trap levels are filled and a non-equilibrium state occurs. In the second step, the voltage pulse is removed and the trapped carriers are released as the sample returns to its equilibrium state, giving rise to a transient current which will be recorded. This current is integrated and each data point (ΔQ) of the Q-DLTS spectrum is obtained from the measurements of the charge transient at two successive times t_1 and t_2 from the beginning of the transient: $\Delta Q = Q(t_2) - Q(t_1)$. ΔQ is measured for increasing values of the time window τ, with

$$\tau = (t_2 - t_1)/\ln(t_2/t_1) \tag{1}$$

The Q-DLTS spectrum is generated by plotting the different ΔQ values as a function of τ. Providing that the charge transient is an exponential function of time, ΔQ can be written as for a single trap:

$$\Delta Q = Q_o[\exp(-e_{p(n)}t_1) - \exp(-e_{p(n)}t_2)] \tag{2}$$

where Q_o is the total amount of charge trapped during the filling pulse ΔV and $e_{p(n)}$ the hole (electron) emission rate of the trap given by

$$e_{p(n)} = \sigma \Gamma T^2 \exp(-E_a/kT) \tag{3}$$

E_a and σ are the activation energy and capture cross section of the trap, respectively. In Eq. (3), k is the Boltzmann constant, T the absolute temperature and Γ a constant. Providing that the ration t_1/t_2 is constant, it is easy to show that ΔQ goes through a maximum value when the window rate τ_m^{-1} matches the emission rate of the trap $e_{p(n)}$ at the measurement temperature. By measuring ΔQ as a function of τ for different temperatures the trap parameters σ and E_a are extracted as the intercept and the slope of an Arrhenius-type plot of $\ln(\tau_m^{-1}/\Gamma T^2)$ versus $1/kT$.

3. Results and discussion

A typical *I–V* characteristic is shown in Fig. 1. The forward current corresponds to a positive bias applied to the ITO substrate. A good rectifying behavior is observed on all the samples studied. Previous investigations in similar devices using different cathode metals indicate a strong dependency of the electrical characteristic on the nature of the cathode, but a true Schottky behavior was not observed [10]. Instead, it was found that the organic layer reacts with the metal to form metallic oxide complexes at the interface, which obviously

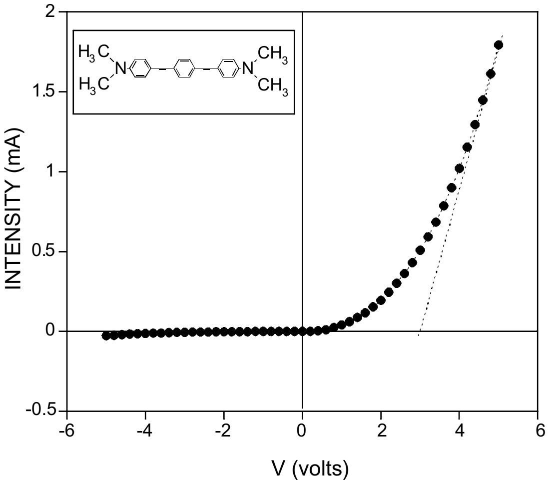

Fig. 1. Typical *I–V* characteristic of ITO-DMASB-MgAg diodes measured at room temperature.

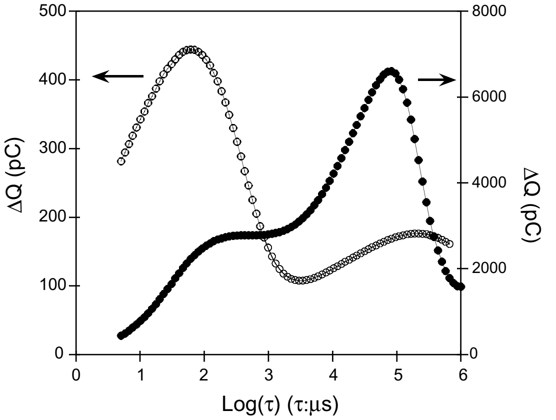

Fig. 2. Q-DLTS spectra measured at room temperature using an offset voltage $V_0 = 0$, a charging time $\tau_c = 1$ s, a charging voltage $\Delta V = +5$ V (black symbols) and -5 V (open symbols).

determine the charge injection process at the cathode.

The Q-DLTS spectra recorded in ITO-DMASB-MgAg samples depend on the applied voltage and its polarities. Fig. 2 shows the Q-DLTS spectra obtained at room temperature with an offset voltage $V_0 = 0$ and a charging voltage $\Delta V = \pm 5$ V of charging time $\tau_c = 1$ s. In both cases, two peaks are clearly visible. The peak labeled peak A, has an emission rate of ~5000 s^{-1} at 300 K while the peak labeled peak B, has an emission rate of ~11 s^{-1} at 300 K. Peak B is dominating the spectrum when a forward bias is applied while peak A is the major peak when a reverse bias is applied. It can be concluded that there are at least two types of traps in DMASB, denoted as types I and II, corresponding to the observed peaks. We note that traps of type I are filled in both directions when the applied voltage is sufficient while traps of type II are predominantly filled in the forward direction with an applied charging voltage higher than 3 V. Furthermore, investigation of the dependence of peak B on both V_0 and ΔV (not shown) revealed that this peak started saturating for a charging voltage higher than 3 V. In the forward direction, the turn-on voltage of the studied diodes is $V_{to} \sim 3$ V. Since electroluminescence takes place when both electrons and holes are present in the emitting layer, the turn-on voltage corresponds to injection of minority carriers (i.e. electrons since DMASB is a p type material) from the cathode, which enables light emission in the devices. Note that if traps are present, these carriers will first fill a specific trap level before electroluminescence could take place. Therefore, the type II traps can be supposed to be filled by electrons and to be donor-like electron traps. In contrast, the type I traps are filled in both forward and reverse directions and therefore can be identified as majority carrier trapping centers (acceptor-like hole traps).

The trapping center parameters were determined by performing measurements at different temperatures between 100 and 315 K. Since the position of the peaks is dependent on both the applied voltages V_0 and ΔV, the traps parameters were determined using a range of V_0 and ΔV values and then compared.

For type I traps, different bias conditions (displayed in Table 1) were used to determine the parameters. Fig. 3 shows the Q-DLTS spectra obtained for the bias condition 2 for different temperatures in the range 260–310 K. At lower temperatures in the range 100–250 K no new peak was observed suggesting that there are no shallow traps in the organic material. The Arrhenius-type plot of $\ln(\tau_m^{-1}/\Gamma T^2)$ versus $1/kT$ for the bias conditions 1–3 are displayed on Fig. 4. The trapping center parameters of peak A in the different bias conditions are reported in Table 1. As seen on

Table 1
Bias conditions used for the analysis of peak A and trap parameters extracted from the measurements

Bias conditions	V_0 (V)	ΔV (V)	τ_c (ms)	E (eV)	σ (cm^2)	N_t (cm^{-3})
Bias 1	0	+1	50	0.38	5×10^{-17}	1×10^{16}
Bias 2	0	−0.5	10	0.37	3×10^{-17}	4×10^{15}
Bias 3	0	−5	10	0.38	1×10^{-16}	2×10^{16}

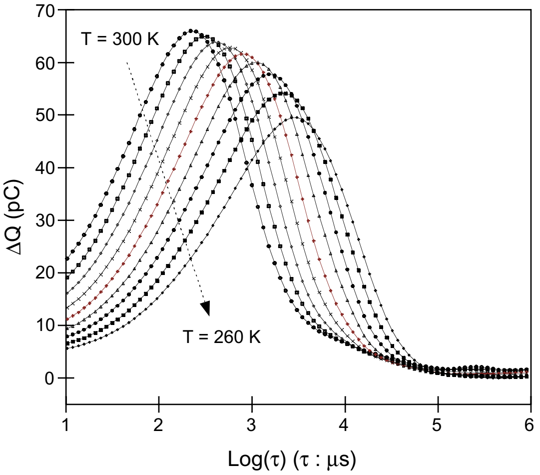

Fig. 3. Q-DLTS spectra measured using an offset voltage $V_0 = 0$, a charging time $\tau_c = 10$ ms, a charging voltage $\Delta V = -0.5$ V for different temperatures in the range 260–300 K.

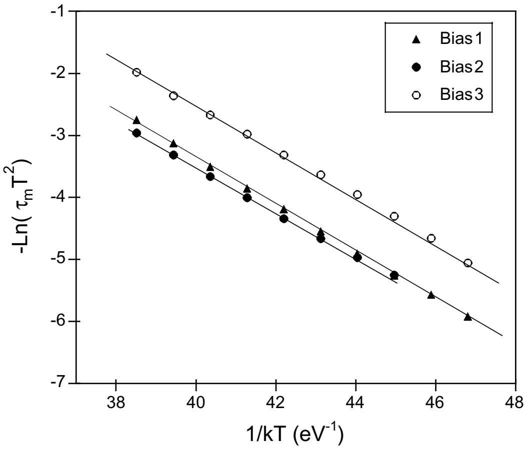

Fig. 4. Arrhenius-type plots of $\ln(\tau_m^{-1}/\Gamma T^2)$ versus $1/kT$ for the different bias conditions displayed in Table 1.

Fig. 4 and Table 1, the trapping center parameters are very similar for the different bias conditions used. This result indicates that the filling process of the type I traps is independent of the bias condition. However, a careful analysis of the shape of peak A for the bias condition 3 indicates that it is roughly twice wider than peak A in bias conditions 1 and 2. Moreover, some shoulders are present on peak A for the bias condition 3. These two observations indicate unambiguously that peak A in the bias condition 3 is not due to a single level contribution but most probably to the contribution of at least three levels. Note that the trap density N_t derived from the height of the Q-DLTS peak for each condition corresponds to the (neutral) filled traps and depends on the charging voltage.

For the type II traps, the trap parameters as extracted from an Arrhenius-type plot of $\ln(\tau_m^{-1}/\Gamma T^2)$ versus $1/kT$ are $E_a \sim 0.50$ eV and $\sigma \sim 10^{-19}$ cm^2. The trap density is $N_t \sim 10^{17}$ cm^{-3}.

Previous defect state studies have been performed on PPV and its derivatives using different techniques [3,4,12–16]. Discrepancies in the trap parameters have been observed in PPV based diodes and might be due to the differing quality of the polymers used. In addition, in these studies, the distinction between minority and majority charge carrier traps was not unambiguously established. Recently, Campbell et al. [7], using a standard DLTS technique, found discrete traps of the acceptor type in PPV with a depth of 0.75 eV and a density of 5×10^{17} cm^{-3}. They assigned these traps to the presence of water or/and oxygen that could contaminate the polymer films during their formation. It is known that residual oxygen released during the conversion of PPV can be incorporated to its backbone, forming carbonyle like bonds by breaking the vinylene linkage of the polymer chains. Gaudin et al. [10] demonstrated that it was possible to distinguish between hole traps and electron traps in PPV based devices using the Q-DLTS technique. The hole traps have activation energies lying in the range 0.49–0.53 eV from the highest occupied molecular orbital (HOMO) and a capture cross section of the order of 10^{-16}–10^{-18} cm^2, while the electron traps are located in the range 0.40–0.42 eV from the lowest unoccupied molecular orbital (LUMO) and have a capture cross section of the order of 10^{-19} cm^2. Similarly, in poly(2-methoxy,5 ethyl(2′-hexyloxy)-1,4-phenylene vinylene) or MEH-PPV based diodes, Stallinga et al. [6], by using a capacitance transient technique, determined four trap levels in the band gap of the polymer. Two majority charge carrier or hole traps located at 0.30 and 1.0 eV from the HOMO and two minority charge carrier or electron traps located at 0.48 and 1.3 eV from the LUMO. Again, the trap parameters determined in this study differ significantly from those obtained by other groups [15,16], presumably because of the varying quality of the materials used.

The nature of traps in organic materials can be considered in terms of chemical impurities or structural defects or both. In a series of articles on trap determination in several organic materials [1,17–20], the Darmstadt group has put forward the hypothesis which favors the importance of structural defects on the formation of traps on the basis of TSC measurements. According to their results, the trap parameters are strongly dependent on structural differences, which can be produced inside an organic material, during the deposition process [20]. They did not however rule out the existence of chemical processes affecting the structure of the material, resulting in new trap states [18]. In the case of PPV and their derivatives, a comparison between trap data allows some similarities in the trap parameters to be revealed. In fact, PPV and the derivative polymers have a backbone composed of phenylene and vinylene units, bonded together through the vinylene linkage. It was demonstrated by several studies that this type of bonding may be broken, creating defect centers in the polymers [21–23]. In the case of DMASB, it was further shown that amine groups, which are bonded to the phenyl rings of the molecule, can be partially broken and replaced by amide ones [24]. These defects are not present in the PPV structure where vinylene linkages are more likely to be affected by chemical reactions to form carbonyl bonds [25]. By comparing Q-DLTS results obtained from PPV samples [10] with those obtained in this study from DMASB, a reasonable hypothesis is to suppose that type I traps are mainly due to deep levels related to amine groups. This, however, does not rule out the presence of additional traps resulting from broken vinylene linkages and contributing to the trap levels of type I (at least three) observed from the Q-DLTS spectra of the DMASB.

Regarding the type II traps, which are electron ones, their assignment in PPV and DMASB was based upon a direct correlation between the onset of electroluminescence and the filling of a new trap (type II) in the Q-DLTS spectrum. Both materials were found to contain carbonyl containing species arising from the oxidation process of the vinyl double bonds. These species are electron accepting species and are likely to act as electron traps in these materials. Nevertheless, it can be further noted that amide groups are also present in the DMASB, which could potentially trap electrons present in the thin film.

The schematic band diagram of the ITO-DMASB-MgAg devices is displayed in Fig. 5. The different energy parameters of the organic material were determined by appropriate techniques, which will be published elsewhere [26]. The energy levels of the traps are supposed to be constant

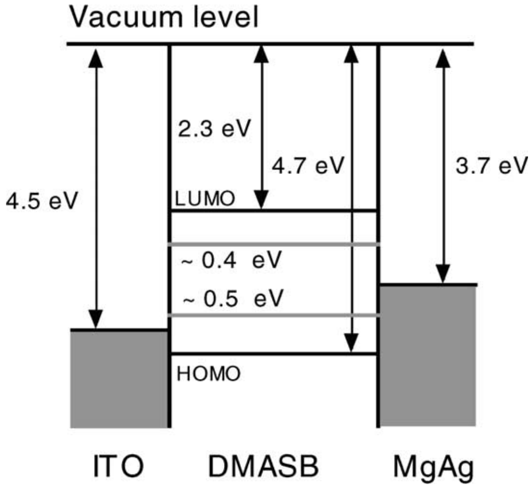

Fig. 5. Band energy diagram of the ITO/DMASB/MgAg devices with trap energy levels determined by the Q-DLTS technique.

throughout the bulk of the DMASB film, but it should be borne in mind that interface states are probably present and may modify the aspect of the energy repartition in these regions.

4. Conclusion

Using the Q-DLTS technique, we have investigated the trap parameters in light emitting diodes based on 4,4′-bis(4-dimethylaminostryryl benzene) (DMASB), a PPV derivative containing amine groups. Analysis of the spectra obtained with different bias and temperature conditions showed that two main trap levels corresponding to two different type traps exist within the band gap of the organic material. Type I traps are assigned to acceptor-like hole traps with a mean energetic level located at 0.38 eV from the valence band. The traps would be distributed over a large energy range centered on its mean level. Type II traps are donor-like electron traps with a mean energetic level located at 0.50 eV from the conduction band. When considering the structure of PPV and DMASB and comparing the Q-DLTS results obtained in both materials, we suggest that the type I traps are probably associated with the amine groups.

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