



Research paper

Molecular vibrations, activation energies of trapped carriers and additional structure in thermoluminescence of organic polymers

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ABSTRACT

Manifestations of optical vibrations in thermoluminescence of organic polymers were observed. Thermoluminescence curves and Raman spectra of the polymers which have different degrees of ordering: poly(di-*n*-hexylsilane), poly(methylphenylsilane) and poly(di-*n*-pentylsilane) were measured and the features on thermoluminescence curves were observed. Activation energies of localized charge carriers were found by the fractional thermally stimulated luminescence in the 5–50 K temperature range. The shape of the thermoluminescence curve was calculated in the model which assumed that the release of carriers from traps may be activated via the energy transfer from the vibrations to the carriers. The model explained the appearance of the features on thermoluminescence curves and the coincidence of the carriers' activation energies with the vibration quanta. Thermoluminescence shows (and the calculations support this claim) that the decrease of the degree of the polymer ordering causes a decrease of the number the discrete values of activation energies and of the number of the features on thermoluminescence curves.

1. Introduction

The release of trapped charge carriers is one of the key processes contributing to the formation of the thermally stimulated luminescence (TSL). In a number of papers devoted to the study of TSL in polymers, assumptions were made, strengthened by arguments, that molecular movements play a role in the carrier release [1–9]. Molecular relaxations were assumed to stimulate the release of charge carriers from traps (which was referred to as the “shake off”). The authors of the paper [8] showed that the activation energy of polystyrene doped with pyrene correlated with three (β -, γ -, and δ -) molecular relaxations of the polystyrene polymer chain. Direct manifestation of optical vibrations in TSL processes was obtained in the experiments [10,11]. These experiments, using the improved fractional TSL method, revealed that certain activation energies of charge carrier traps in the silicon organic polymer poly(di-*n*-hexylsilane) (PDHS) were discrete and coincided with the energies of molecular vibrations' modes observed in the Raman spectrum of the polymer. The earlier study of the distribution of trapped charge carriers in π - and σ -conjugated polymers by the fractional TSL method showed the existence of a quasi-continuous trap distribution [12–14]. The distribution of levels may consist of a sum of the levels of several types of traps, but due to fluctuations of positions and

orientations of molecules these levels are broadened and overlap, thus the spectrum of the polymer becomes quasi-continuous. The model suggested in [11] for the interpretation of this phenomenon cannot explain the coincidence of the activation energies with the energies of vibrations. Therefore, the following model was proposed in [15] for the explanation of this coincidence. After the irradiation of a sample and producing localized carriers there, the system is brought to a non-equilibrium state, with the vibrational subsystem coming to the equilibrium earlier than the electronic. As a result, the vibrations are in equilibrium, while the charge carriers are still on traps. Within the system, the energy of vibration quanta may be transferred to carriers, releasing the latter from traps. Usually this process involves the participation of many vibrations, leading to the Arrhenius formula for the probability of the carrier release from a trap ($\exp(-E_a/kT)$), where E_a is the trap depth and T is the temperature. In our model, we consider the process in which the release of the carrier from the trap occurs via a single-phonon process, when the energy of the optical vibration's quantum is transferred to the carrier. According to the energy conservation law, such process is possible if the vibration's energy is equal to or greater than the trap depth. Taking into consideration such processes in [15] made it possible to explain the coincidence of the carrier's activation energies observed in TSL in [10,11] with those of vibration's

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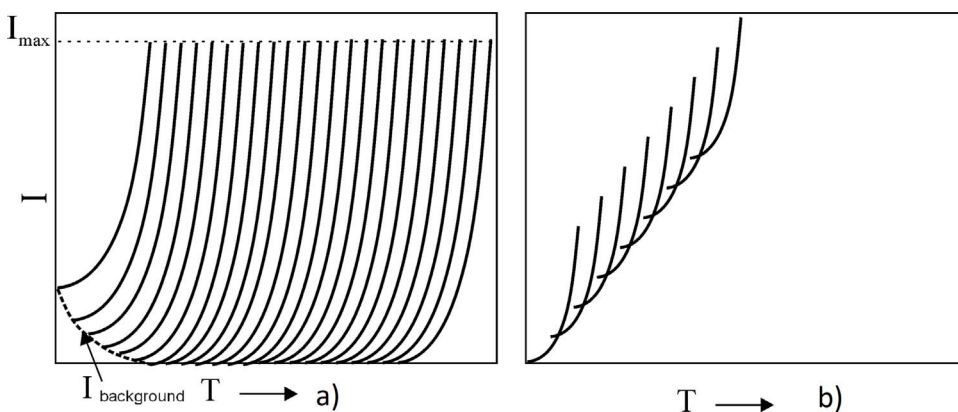


Fig. 1. Regime of the temperature modulation: a) – our method, b) – traditional method [22,23].

quanta, observed in the Raman spectrum [16–18] and to predict the appearance of features in the shape of TSL curve. In the work [19], the additional activation energies for traps in the PDHS were found by the fractional TSL method. The structure caused by vibrations would manifest itself as spikes and dips on the TSL curve. The heights of spikes and the depths of dips are determined by the interaction of the carrier localized on a trap with the vibration's quantum. If the interaction is weak, the structure should vanish. The discrete values of the activation energies and additional structure on TSL curves should also depend on the degree of the ordering of the polymer. The degree of the ordering (or “degree of crystalline order” [20] is the ratio between trans- and gauche- conformations of polymer chains) influences the width of the vibrational bands, which plays an important role in the suggested model. Therefore, the ordering should manifest itself in the investigated effects as the appearance of discrete activation energies and the additional “structure” on the TSL curve. To verify this, TSL and Raman spectra of polymers with varying degrees of ordering were studied.

Therefore, in this paper, we looked for and detected discrete values of activation energies and predicted additional features on the TSL curves for several types of silicon organic polymers with varying degree of ordering: poly(di-*n*-hexylsilane) PDHS, poly(methylphenylsilane) PMPS and poly(dipentylsilane) PDPS. The investigation of the manifestation of vibrations in TSL and the observation of the additional structure may give information about the trapping centers in the polymers. (It is known that a great deal of information is obtained by studying electron-vibration spectra of defects). The additional features on the TSL curves are weak, so in order to ensure that they are not induced by noise, the measurements were carried out for three substrates: metal, sapphire and quartz. To do this, the fractional TSL method was used to determine the activation energies of traps, and the Raman spectra were measured for the same samples. Additionally, the TSL curve was calculated taking into account the effect of several types of vibration modes with variable width of vibration lines and compared with experiment.

2. The experimental technique

PDHS, PMPS or PDPS polymer films were prepared as follows. The polymer powder was dissolved in toluene with the concentration of 10^{-3} mol/l and kept for a day in dark at room temperature. Further, polymer solutions were deposited by direct casting on different substrates (sapphire, metal or quartz) and were kept for a day to remove the solvent. It is known that PDHS precipitation from toluene yields a crystalline structure with an all-trans backbone at room temperature [20]. Since the crystalline structure of PDHS films varies greatly with crystallization conditions (type of the solvent, temperature, annealing treatment or UV irradiation) [20,21], polymer films with different degree of ordering were prepared at identical conditions.

TSL measurements were carried out with the automatic equipment

for optical thermally stimulated spectroscopy over the temperature range from 5 to 150 K with the heating rate of $\beta = 0.25$ K/s. Freshly prepared films with the thickness of 5 μm were used. The samples were cooled to the liquid-helium temperatures either slowly (with a rate of ~ 20 K/min) or rapidly (with rate of 295 K/min). All figures of the TSL curves are given for polymers cooled by slow cooling. The carriers in the polymers were photogenerated by exciting the samples with unfiltered light of an Hg lamp for 2 min at 5 K.

The fractional TSL method involves detection of the emission intensity of the sample pre-excited at low temperature during its gradual linear heating over a small temperature range followed by immediate cooling. Cyclically repeated heating-cooling continues till the traps are totally emptied. The estimation of the activation energy of the traps is based on the assumption that the filled traps' concentration is practically unchanged during a current heating process (1–5 percent of the existing filled traps). Activation energies of traps were calculated by the equation usually used in the TSL analysis

$$E = -k_B \frac{\Delta(\ln I)}{\Delta\left(\frac{1}{T}\right)} \quad (1)$$

The fractional TSL method allows obtaining sets of data for trap energies of an excited sample which significantly increases the reliability of the results. The important advantage of the method is that the calculated activation energies are independent of the TSL kinetics. The following regime of the temperature modulation was used: the sample was cooled down to the temperature at which the glow intensity attained its minimum value (subsequently it is referred to as the background emission intensity, Fig. 1a). The initial slope was registered until the signal intensity reached the value I_{max} (Fig. 1a). The full dynamical range of the detection system was used to register every fraction. Under such conditions, the number of the fractions obtained is limited only by the detection system's sensitivity rather than the capacity of the analog-digital signal converter. The TSL intensity of the studied polymers is quite high. This makes it possible to increase the registration system's sensitivity by 2–3 orders of magnitude as compared with that used for the detection of the integral TSL curves of other polymers. As a result, the technique permits to obtain more than 85 heating fractions in the temperature range of 5–50 K. As noted, the maximum numbers of fractions obtained using traditional methods [22,23] did not exceed 20–30 fractions in the temperature range of 5–100 K (Fig. 1b). This substantially reduces the resolution of such methods. It should be noted that the measurement of the dark signal before and after each fraction revealed that TSL was accompanied by some background glow (the intensity of the background glow is shown in Fig. 1a) which is of tunneling nature that is not directly associated with thermal emptying of the traps. Its level slowly decreases from fraction to fraction. More details of the procedure may be found in Ref. [10,11].

It is known that PDHS has a reversible thermochromic transition at

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