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(980-8578 Sendai, Japan)**INTERACTION OF OPTICAL
VIBRATIONS WITH CHARGE TRAPS
AND THE THERMOLUMINESCENCE
SPECTRA OF POLYMERS**

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The energy spectrum of hole traps is investigated in organic polymer poly(di-n-hexylsilane) by the fractional thermally stimulated luminescence (TSL) in the 5–40 K temperature range. In addition, the Raman spectrum of the polymer is studied at 300 K. For the first time, the structure on a TSL curve is observed. It is found that the obtained activation energies of traps coincide with the frequencies of Si–Si vibrations of the polymer chain active in the Raman spectra. These results have been explained within a model, by which the release of charge carriers from traps may be activated via the resonant energy transfer from Si–Si vibrations to the charge carriers. The model explains the appearance of a structure on the TSL curve.

Keywords: poly(di-n-hexylsilane), traps, thermoluminescence, Raman spectra, activation energy.

1. Introduction

Poly(di-n-hexylsilane) (PDHS) is a silicon organic polymer, which consists of the σ -conjugated Si-backbone and hexyl side groups (Fig. 1).

Due to the delocalization of σ -bonds in the Si-backbone (30 atoms in length [1]), PDHS has several unique photophysical characteristics, namely: strong absorption in the UV range, high quantum fluorescence yield and high hole mobility. These characteristics determine the possibility of its usage as transport [2] and light-emitting layers [3] in electroluminescent devices. A PDHS macromolecule, which consists from the segments of different lengths, has mainly an ordered trans-conformation (all-trans or anti-trans) at room and lower temperatures. Under real conditions, the anti-trans conformation of the polymer chain is

disturbed by the rotation of a polymer chain segment around the Si–Si bonds; i.e., by a formation of the conformational defects [4]. These defects create the energy barriers for holes, so that, at low temperatures, the hole is delocalized within a segment. Thus, silicon organic segments of different lengths are the traps for holes. The model of quasicontinuous distribution of traps in polymers [5–7] is accepted nowadays.

The study of the fractional low temperature thermally stimulated luminescence (TSL) provides important information about the presence and the nature of traps and defects for charge carriers. One of the processes determining the properties of TSL is charge carriers' escape from traps. In order to leave a trap and to transit to a state with the energy above the mobility threshold, a charge carrier has to acquire some additional energy.

Studies of polymers in a number of papers have revealed a connection between TSL processes and

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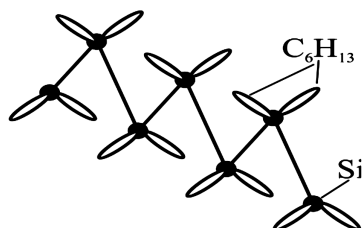


Fig. 1. Structure of PDHS polymer

the processes of molecular relaxation: motion of the molecular groups connected to the polymer backbone and other similar processes [8–15]. Thus, the effect of movements of various fragments of the molecule on TSL spectra was established in a number of studies. At the same time, the molecular vibrations manifest themselves in various optical properties of polymers: in absorption, luminescence, and Raman scattering. The connection between the activation energies of the traps of charge carriers and the energies of optical vibrations of the polymer backbone observed in the Raman spectra [16, 17] has been recently obtained in [18, 19], by using the TSL spectra of PDHS films. A model was proposed in [20] for the explanation of these results. It was assumed that the processes of release of holes from traps are activated via the resonant energy transfer from Si–Si vibrations of the polymer chain that are excited, as the temperature increases, to charge carriers. Note that the model also predicts the appearance of a structure on the TSL curve.

Therefore, we focus herein on the detailed correlation between the activation energies of hole traps and the frequencies of Si–Si Raman modes of the polymer chain in the low-temperature region of TSL spectra, as well as on the TSL curve structure. To provide this correlation, the TSL spectrum of PDHS at 5–40 K and the Raman spectrum of the same polymer at 300 K were investigated. It was found that the TSL curve has a fine structure, and the energy spectrum of traps consists of six horizontal shelves, which coincide with the frequencies of Si–Si vibrations of the polymer chain, active in the Raman spectra. The results are the experimental confirmation of the proposed model.

2. Experimental Technique

The fractional TSL measurements were carried out with an automatic equipment for optical thermally stimulated spectroscopy over a temperature range

from 5 to 40 K with the heating rate $\beta = 0.25$ K/s. The PDHS films were prepared by the direct casting from a toluene solution on sapphire substrates. Freshly prepared PDHS films with a thickness of $5 \mu\text{m}$ were used. The charge carriers in PDHS were photo-generated by the sample excitation by unfiltered light of a Hg lamp for 2 min at 5 K.

The fractional TSL method involves the detection of the emission intensity from the sample pre-excited at a low temperature under its linear heating over a small temperature range followed by the immediate cooling. The cyclically repeated heating-cooling continues up to the total trap emptying. For the initial part of the TSL curve (corresponding to 1–5 per cent of the existing filled traps), the concentration of filled traps is small and can be neglected. The activation energy of traps was calculated by the formula usually used in the TSL analysis:

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

The fractional TSL method enables us to obtain a set of data for energies of a singly excited sample, which significantly increases the reliability of the results. The important advantage of the method is that the calculated 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 (which is subsequently referred as the background emission intensity). The initial slope was registered until the signal intensity reached the value specified by the program. 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 sensitivity, rather than by the capacity of an analog-digital signal converter. The TSL intensity of the studied polymer is quite high. This makes it possible to increase the registration 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, this allows one to get more than 85 heating fractions in the temperature range of 5–40 K. It was noted that the maximum number of fractions within the traditional methods [21, 22] was not more than 20–30 fractions in the temperature range

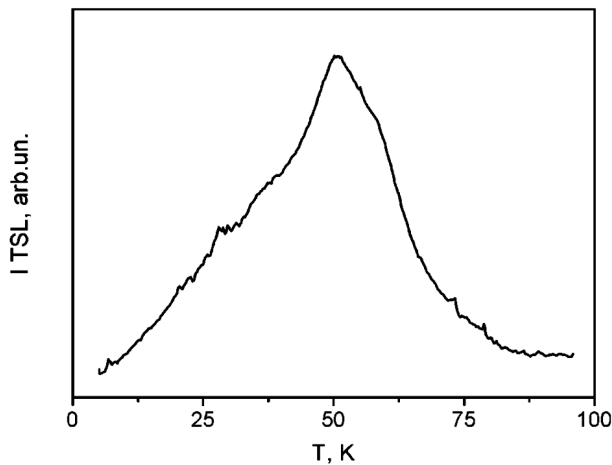


Fig. 2. TSL curve of a PDHS film

of 5–100 K. This substantially reduces the resolution of those methods. More details of the procedure may be found in Ref. [18, 19].

The resonance Raman spectra were excited with the radiation of an Ar–Kr ion laser line (514.5 nm) at 300 K and were measured in the back scattering geometry using a triple Raman spectrometer T-64000 Horiba Jobin-Yvon equipped with a charge coupled device (CCD) detector. The spectral resolution was about 0.1 cm^{-1} . To avoid the sample heating, the power through the objective always was under 1 mW.

3. Experimental Results.

Determination of the Activation Energy of the Charge Carrier Traps

In Fig. 2, the solid line shows the integral TSL curve for a PDHS film. As seen from Fig. 2, the TSL curve is represented by a broad band with a maximum at 50 K. It should be emphasized that the additional structure is clearly observed on the TSL curve. The structure consists of small dips and wells on the curve and cannot be considered as a noise, because it is repeated in the re-recording. Figure 3 shows the Raman spectrum of a PDHS powder at 300 K excited by a laser line at 514.5 nm. Figure 4 shows the dependence of the activation energy of traps on the fraction number measured in the 5–40 K temperature interval. The numbers on the horizontal shelves show the activation energies in eV. The frequencies of the Raman spectrum in cm^{-1} are given in brackets. It is

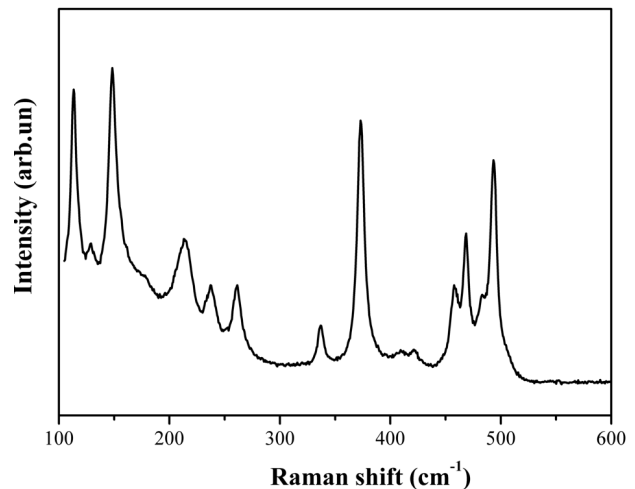


Fig. 3. Raman spectrum of a PDHS powder at 300 K. (Resolution = 0.1 cm^{-1} , $\lambda_{\text{ex}} = 514.5 \text{ nm}$.)

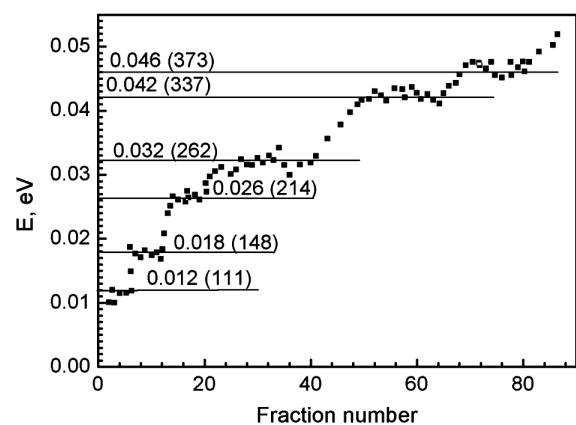


Fig. 4. Dependence of the activation energy of traps on the fraction number in the 5–40 temperature interval. The numbers on the horizontal shelves show the activation energies in eV. The frequencies of the Raman spectrum in cm^{-1} are given in brackets

seen that the activation energies of traps form six horizontal shelves: 0.0122 ± 0.0005 , 0.0181 ± 0.0003 , 0.0262 ± 0.0002 , 0.0324 ± 0.0002 , 0.0418 ± 0.0003 , and $0.0462 \pm 0.0005 \text{ eV}$. The comparison of the data obtained in the study of the TSL and Raman spectra (see Fig. 4) shows that the activation energies of traps correlate well with the frequencies of Si–Si vibrations of the polymer chain: 111 cm^{-1} (0.012 eV), 148 cm^{-1} (0.018 eV), 214 cm^{-1} (0.026 eV), 262 cm^{-1} (0.032 eV), 337 cm^{-1} (0.042 eV), and 373 cm^{-1} (0.046 eV), respectively.

This result allows us to conclude that, although the energy spectrum of traps is the quasicontinuous, the release of holes in the polymer in the proposed model is more probable from those traps, whose depth corresponds to the energy of Si–Si vibrations of the polymer chain.

In addition, we detected an additional structure on the TSL curve (Fig. 2), which was predicted by the model developed in [20]. The model suggested in [19] cannot explain the coincidence of the activation energy with the energy of vibrations. Therefore, we use the model suggested in [20], which explains this coincidence and predicts the appearance of the structure.

4. Base of the Model and Discussion

The system of charge carriers captured by traps after the irradiation is non-equilibrium. The equilibration in the vibration subsystem happens much faster than the equilibration in the electronic subsystem (in the charge distribution). So, we may suggest that the vibration subsystem is in the equilibrium state, but the electronic subsystem is non-equilibrium. Under such condition, there is a process, in which energy of vibration quanta may be transferred to a trapped carrier and pulls out it to the state above the mobility threshold. This occurs if the localization center has trapped energy coinciding or less than the vibration quantum energy. Subsequently, the carrier recombines with a charge of opposite sign and manifests itself in TSL.

The interaction of a localized charge carrier with the single vibration mode may be presented by the formula

$$U(\mathbf{r}, q) = U(\mathbf{r}, 0) + \sum_{\alpha} \left. \frac{\partial U(\mathbf{r}, q)}{\partial q_{\alpha}} \right|_{q=0} q_{\alpha} + \frac{1}{2} \sum_{\alpha, \beta} \left. \frac{\partial^2 U(\mathbf{r}, q)}{\partial q_{\alpha} \partial q_{\beta}} \right|_{q=0} q_{\alpha} q_{\beta}, \quad (2)$$

where $U(\mathbf{r}, q)$ is the interaction of the trapped charge carrier with the polymer matrix, r is the coordinate of the trapped charge, q designates the normal coordinates of nuclei, and α designates the type of vibrations. Considering the second term as a perturbation, we obtain the following expression for the per-unit-time probability for an electron to transit from the

state i to the state j with a simultaneous absorption of the energy $\hbar\omega_{\alpha}$ of an α -type vibration:

$$P_{i,j}^{\alpha} = w_{i,j}^{\alpha} N(\hbar\omega_{\alpha}, T) \delta(\hbar\omega_{\alpha} - E_j + E_i), \quad (3)$$

where E_i and E_j are the energies of initial and final states of the carrier, δ -function determines the energy conservation law, $w_{i,j}^{\alpha} = \frac{2\pi}{\hbar} \|V_{i,j}^{\alpha}\|^2$, $V_{i,j}^{\alpha} = \langle j | \left. \frac{\partial U(\mathbf{r}, q)}{\partial q_{\alpha}} \right|_{q=0} | i \rangle / 2$, and $N(\hbar\omega_{\alpha}, T) = 1 / (\exp(\frac{\hbar\omega_{\alpha}}{\kappa T}) - 1)$ is the Bose–Einstein distribution for vibrations.

The probability for the charge carrier with initial energy E to escape from a trap after obtaining the energy $\hbar\omega_{\alpha}$ from a vibration may be obtained from (3) after the summation over the final states

$$P_{E,\alpha} = W(E, \alpha) N(\hbar\omega_{\alpha}, T), \quad (4)$$

where $W(E, \alpha) = w_{E, \hbar\omega_{\alpha} + E}^{\alpha} g_0(\hbar\omega_{\alpha} + E)$, $w_{E,E'}^{\alpha}$ is the charge carrier transition probability from the state with energy E into the unit interval of energy in a vicinity of the energy E' , and g_0 is the energy density of final states.

We considered the trapped state dynamics and marked out the processes of release of charge carriers accompanied by the absorption of vibration quanta separately from all other processes, the probability of which are described by the Arrhenius formula. In this case, the time dynamics of charge carrier's density may be presented in the form

$$\frac{dn(E, T)}{dE} = -n(E, T) \times \begin{cases} W(E, \alpha) N(\hbar\omega_{\alpha}, T) + \\ + P \exp(E/kT), & |E| < \hbar\omega_{\alpha}, \\ P \exp(E/kT), & |E| > \hbar\omega_{\alpha}, \end{cases} \quad (5)$$

where $n(E, T)$ is the number of localized charges in a unit interval of the energy, and E is the energy of a trapped carrier with respect to the mobility threshold ($E < 0$). The term $W(E, \alpha) N(\hbar\omega_{\alpha}, T)$ describes the process of localized charge carrier release with the absorption of a vibration quantum. The $P \exp((E/\kappa T))$ term describes the contribution from the processes involving all other vibrations, including multiphonon processes, to the processes of charge carrier delocalization.

After the solution of Eq. (5), we obtain the temperature dependence of the radiation intensity:

$$I(T) = -C \frac{dN(t)}{dt} =$$

$$\begin{aligned}
&= C \int_{-E_i}^0 dE n_0(E) \left[W(E, \alpha) N(\hbar\omega_\alpha, T) + P e^{E/kT} \right] \times \\
&\times \exp \left\{ -\frac{1}{b} \int_{T_0}^T \left[W(E, \alpha) N(\hbar\omega_\alpha, T') + P e^{E/kT'} \right] dT' \right\} + \\
&+ C \int_{-\infty}^{-E_i} dE n_0(E) P e^{E/kT} \exp \left\{ -\frac{1}{b} \int_{T_0}^T P e^{E/kT'} dT' \right\},
\end{aligned} \tag{6}$$

where C is a constant, $N(t)$ is the total number of trapped charges, and $b = \frac{dT}{dt}$ is the heating rate.

The examples of TSL curves for several types of vibrations are presented in [20].

The analysis shows that, in the disordered system, 1) the activation energies coincide with the energies of vibration quanta, and 2) a structure arises on the TSL curve in the form of dips and wells. The intensity of radiation (4) contains the value of vibration number $N(\hbar\omega_\alpha, T)$. Usually, the condition $\hbar\omega_\alpha \gg \kappa T$ takes place in experiments. In this case, $N(\hbar\omega_\alpha, T) \sim \exp(-\hbar\omega_\alpha/\kappa T)$. So, the contribution of vibrations to the charge carrier escape (3) has the form, which is similar to the contribution of the trap, but the vibration quantum energy plays the role of activation energy. Therefore, though many traps are present in the system (spectrum of the polymer is quasicontinuous), only several of them, whose energies of activation are in resonance with vibration quanta, give the studied effect on TSL. The manifestation occurs in the form of dips and wells in some narrow region of the temperature. The temperature, at which the effect exists, is determined by the value of activation energy and by the kinetic coefficients. At lower temperatures, the structure is absent, because the number of resonance quanta is small. At higher temperatures, the effect disappears, because the other mechanisms of carrier release become more efficient.

5. Conclusions

We have studied the spectrum of hole traps of the silicon organic polymer poly (di-n-hexylsilane) by the low-temperature fractional TSL method in the temperature interval 5–40 K and the Raman spectra of the polymer at 300 K. The coincidence of the trap activation energy with the energies of Si–Si vibrations of

the polymer chain, obtained from Raman spectrum, allows us to conclude that the releases of charges in the proposed mechanism occur only from those traps, the depth of which corresponds to Si–Si vibrations of the polymer chain. In this region of temperatures, the structure on the TSL curve is observed, which was predicted in the model [20].

The proposed model may be applied to other polymers and other disordered condensed matter systems with a continuous spectrum of traps and not too broad width of separate vibration lines, for example, to the amorphous semiconductors, glasses, disordered thin films, and gamma-irradiated materials. The detailed investigation of the effects and their connection with vibrations will provide a tool for extracting the information related to the localization centers and the electron-phonon interaction in the organic systems.

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ВЗАЄМОДІЯ ОПТИЧНИХ
КОЛИВАНЬ З ПАСТКАМИ ЗАРЯДУ І СПЕКТРИ
ТЕРМОЛЮМІНЕСЦЕНЦІЇ ПОЛІМЕРІВ

Резюме

Досліджено енергетичний спектр пасток для дірок в органічному полімері полі(ді-н-гексилсилані) методом термостимульованої люмінесценції (ТСЛ) в інтервалі температур 5–40 К. Також отримано спектр комбінаційного розсіяння (КР) при 300 К полімера. Вперше виявлена структура на кривій ТСЛ. Знайдено, що енергії активації пасток збігаються з енергіями квантів коливань кремнієвого ланцюга, активних в КР спектрах. Ці результати пояснюються на основі моделі, згідно з якою звільнення носіїв з пасток відбувається за рахунок резонансної передачі енергії від Si–Si коливань до носіїв заряду. Модель пояснює наявність структури, що спостерігається на кривій ТСЛ полімеру.