Effect of the polymer ordering on the optical spectra and thermoluminescence of polygermane and polysilane films and nanocomposites

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Comparative study of optical spectra and thermoluminescence of poly(di-n-hexylgermane) (PDHGe) and poly(di-n-hexylsilane) (PDHS) films and nanocomposites with different degrees of ordering have been carried out in the temperature range 5–200 K. The disordering processes, which are essential for PDHGe, lead to the appearance of additional bands in its optical spectra associated with different set of trans- and gauche-conformations of the polymer chain as well as to the broadening of vibrational bands in Raman spectrum. It is shown that polymer chains of confined PDHGe introduced into the nanopores of SBA-15 silica, in contrast to those of PDHS have the gauche-conformation instead of the trans-conformation, as a result of decrease of intermolecular interaction between the polymer chain segments and increase of their mobility. Besides, appearance of discrete levels of the carriers' activation energy in thermoluminescence of both polymers were observed, energies of which coincide with the optical vibration quanta. Disordering processes cause reduction of the number of observed discrete levels of the activation energy for PDHGe.

Keywords: polymetallanes, films, nanocomposites, activation energies, traps, thermoluminescence.

1. Introduction

σ-conjugated $(MR_2)_n$ polymers, where M = Si, Ge, and R is an organic molecule, have unique optoelectronic and electrophysical properties due to the delocalization of σ-electrons along the polymer chain consisting of M atoms. Studies of properties of such polymers attract attention due to their possible application as photodiodes, photoresists and materials for nonlinear optics [1].

One of the most studied silicon organic polymers is poly(di-n-hexylsilane) (PDHS). The degree of the crystallinity of the PDHS polymer reaches 69% [2]. Specific ordering in this material is also confirmed by spectroscopic and x-ray data. Indeed, x-ray reflections in the PDHS are fairly distinct, resembling a crystalline phase [3–5]. IR [6] and Raman [4,7,8] spectra of the PDHS consist of narrow bands like the spectra of crystals.

Poly(di-n-hexylgermane) (PDHGe) has structure similar to that of PDHS, where the monomer unit $Si(C_6H_{13})_2$ is replaced by $Ge(C_6H_{13})_2$. Since the Ge–Ge bond is longer than the Si–Si bond, the intramolecular interaction between segments of polymer chains is expected to be less pro-

nounced [9] as compared with PDHS. This suggests that PDHG has higher flexibility near its backbone, and conformational changes in the polymer chain are more probable for PDHGe than for PDHS. It correlates well with the x-ray data [9] showing that the PDHGe film is less ordered than the PDHS film. This fact also explains differences in the absorption spectra of films of these polymers. Absorption spectrum of the PDHS film consists of two bands, associated mainly with the ordered trans-conformation and a small fraction of the disordered gauche-conformation of the polymer chains. The absorption spectrum of the PDHGe film consists of four bands [10,11], having different ratios of trans- and gauche-conformations along the polymer chain. These data indicate that PDHGe polymer is more disordered comparing to PDHS.

Low-temperature thermoluminescence (TSL) is used to study processes of localization of charge carriers on traps, as well as processes of their release. In order to leave a trap and transit to a state with the energy above the mobility threshold, a charge carrier has to acquire some additional energy. To determine the activation energy of the charge

carriers in polymers, the fractional TSL method has been used. It was previously believed that the dependence of the activation energy of charge carriers on temperature in polymers has a quasi-continuous character [12]. However, in a number of works [13–17] studying PDHS polymer films, these dependences differ from the quasi-continuous character. It was first shown that discrete levels appear in the dependence of the carriers' activation energy on the temperature, and these energy levels coincide with the optical vibrations quanta determined from the Raman spectra. For a freshly prepared PDHS film on a sapphire substrate, whose polymer chains mainly consist of the trans-conformation segments, there were up to 6 discrete levels observed [17]. Based on these studies, the following model of carriers release from the traps was proposed [18]: not only multiphonon processes, but also single vibration may take part in process of charge carriers release from traps. The release of carriers occurs due to an energy transfer from the vibration to the trap as a result of an interaction between the vibration and the carrier. The transfer of energy occurs to those traps of the continuous spectrum, the bond energy of which coincides with the energy of optical vibrations quanta.

It was shown by the repeated TSL measurements of PDHS film [17] that the number of discrete levels of the energy activation decreases. This is apparently associated with a change in the polymer morphology in the result of irradiation. This suggests that the appearance and number of discrete levels in the dependence of the activation energy on temperature depends on the ordering of the polymers.

In the present paper, we study the effect of the polymer ordering on the processes of release of charge carriers localized on traps appearing in the germanium organic polymer PDHGe. For this purpose, comparative studies of the TSL curves and the fractional TSL are carried out for the "crystalline" PDHS and PDHGe having a different degree of ordering. In addition, the influence of the ordering effects on the optical spectra of films and nanocomposites of these polymers is investigated.

2. Experimental procedure

The PDHGe was synthesized as described in [19]. Details of the preparation of the mesoporous silica material SBA-15 was described in [20].

In order to incorporate the PDHG polymer (Mw = 10600) into nanopores of 6 nm SBA-15, the prepared silica matrixes were immersed in a 1 wt% solution of the polymer in toluene and slowly stirred in dark at 293 K for several hours and then kept in dark till evaporation of the solvent. Then the composite was twice washed in dark for approximately 1 h by stirring it in the fresh toluene to remove the polymer from the exterior surface. The location of the polymer in the pores was determined by the x-ray diffraction.

TSL measurements were carried out with automatic equipment for optical thermally stimulated spectroscopy over the temperature range from 5 to 200 K with the heating rate of β = 0.25 K/s. The PDHS and PDHGe polymer films were prepared by direct casting from toluene solution on a metal substrate. Freshly prepared films with the thickness of 5 μm were used. The carriers in the polymers were photogenerated by the samples' excitation 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

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

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). More details of the procedure may be found in [13].

The fluorescence (FL) and excitation spectra of the polymer films on quartz substrates were recorded using a DFS-12 and a Hitachi MPF-4 integrated with a helium cryostat at the temperature of 5 K. The FL was excited with a xenon lamp with the monochromator selected wavelength of 313 nm. The absorption spectra were recorded with a KSVU-23 at room temperature.

3. Results and discussion

3.1. Absorption and fluorescence spectra of PDHGe and PDHS films

Figure 1 shows the absorption spectra measured at room temperature (a) and the FL spectra at *T* = 5 K (b) of the PDHS and the PDHG films. We see that the absorption spectrum of the PDHS film has two bands at 362 and 313 nm assigned to the σ–σ* transitions of the Si backbone (Fig. 1(a), dotted line). These absorption bands are assigned to the polymer chain having ordered trans- and disordered gauche-conformations, respectively. The distance between these bands is 58 nm. The absorption spectra of the PDHGe film
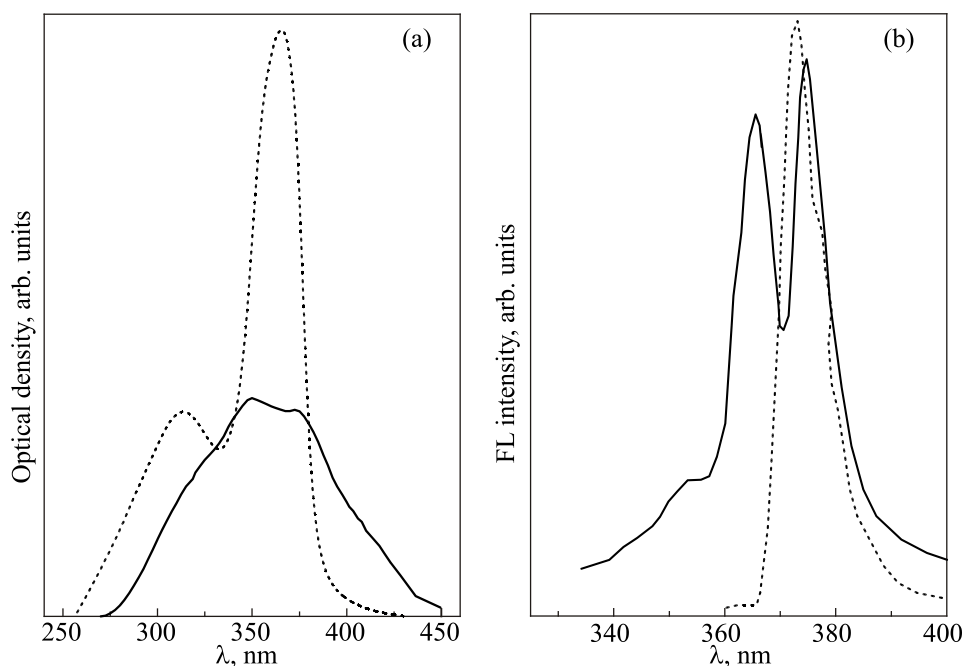
Fig. 1. (a) Absorption spectra of PDHS (dotted line) and PDHGe (solid line) films at room temperature and (b) FL spectra (5 K) of PDHS (dotted line) and PDHGe (solid line) films.

become more structured and consist of four bands with maxima at 373, 348, 335 and 323 nm (Fig. 1(a), solid line). These spectra agree with the data obtained in works [10,11]. It has been shown that the bands at 373 and 323 nm are assigned to the polymer chain having trans- and gauche-conformation, respectively. Distance between these absorption bands is 53 nm, which is almost the same value as for the PDHS film. Other bands in the spectrum originate from the absorption centers with different amounts of gauche- and trans-conformers along of the polymer chains. FL spectrum of the PDHS film ($T = 5$ K) has a single and intense band with maximum at 371 nm (Fig. 1(b), dotted line). FL spectrum of the PDHGe film ($T = 5$ K) is more structured and consists of three bands at 352, 366 and 376 nm (Fig. 1(b), solid line). Appearance of several bands in the optical spectra of the PDHGe film confirms the greater disorder of this polymer comparing to the PDHS film.

3.2. Fluorescence and excitation spectra of PDHGe/SBA-15 and the PDHS/SBA-15 nanocomposites

The FL spectrum of PDHS/SBA-15 nanocomposite with a pore diameter of 6 nm ($T = 5$ K) consists of the single band at 350 nm (Fig. 2(a)). This band is assigned to the polymer chain having the trans-conformation and it is shifted by 21 nm to the short-wavelength region with respect to the trans-conformation band in the FL spectrum of PDHS film [21]. The excitation spectrum of this composite shows a single band with a maximum at 346 nm, which is blue-shifted relative to the absorption band of the trans-conformation of the film by the value of the same order of magnitude (16 nm). This significant blue shift is due to the decrease of the number of polymer chains in the pore and the reduction of the intermolecular interaction between them. This confirms that the polymer chains are indeed incorporated into 6 nm pores.

The FL and excitation spectrum of PDHGe incorporated in SBA-15 with a pore diameter of 6 nm obtained at 5 K are presented in Fig. 2(b). The FL spectrum shows the single band with a maximum at 338 nm, which is also blue-shifted relative to the band of the trans-conformation of the film as in the case of the PDHS/SBA-15 nanocomposite, but by the greater value (38 nm). The excitation spectrum observed for this FL band shows a single band with a maximum at 317 nm, which is significantly blue-shifted relative to the absorption band of the trans-conformation of the film by 56 nm. Since in the absorption spectra of the PDHS and PDHGe films the distance between the trans- and gauche-conformation bands is almost the same (58 and 53 nm, respectively), then the shifts of the bands of the same conformation in the spectra of their nanocomposites should have similar values. This suggests that the conformation of the polymer chains of the confined PDHS differs from that of the PDHGe. If we measure the shift of the FL and excitation bands of the PDHGe/SBA-15 nanocomposite starting from the corresponding bands of the PDHGe film, namely, from the 352 and 323 nm, which originate from the gauche- conformation, we obtain 14 and 6 nm, which are close to the data for PDHS/SBA-15 nanocomposite. So, the result obtained for the PDHS/SBA-15 nanocomposite differs from that for the PDHGe/SBA-15 nanocomposite in
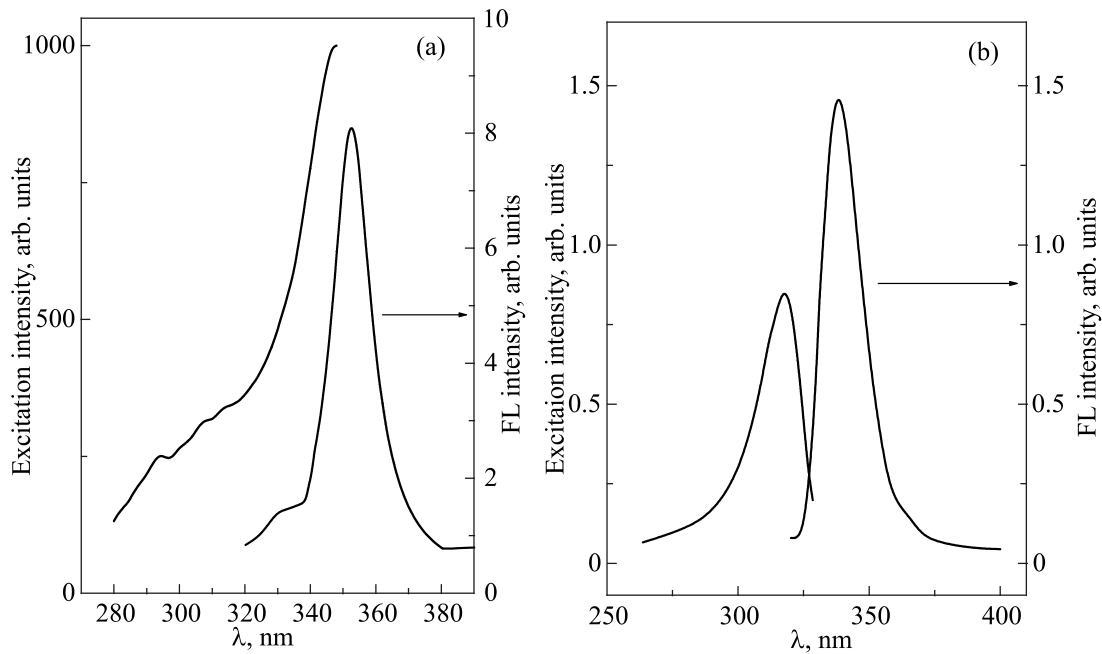
Fig. 2. FL and excitation spectra of the PDHS/SBA-15 nanocomposite (a) and the PDHGe/SBA-15 nanocomposite (b) ($T = 5$ K, a pore diameter of 6 nm).

that significant aspect that the confined PDHS polymer chain has the trans-conformation [21], whereas the confined PDHGe polymer chain has the gauche-conformation due to the greater mobility of the polymer chain segments.

3. Low-temperature thermoluminescence and activation energies of the traps of PDHGe and PDHS films

Figure 3 shows the integral TSL curves for the PDHS films on the metal substrate. It should be emphasized that the additional features referred further as "the structure" are clearly observed on these TSL curves [17]. Figure 4 shows the activation energies of charge carrier detrapping processes for these PDHS films measured in the 8–50 K temperature range [17]. The numbers on the horizontal shelves indicate the activation energies in eV. It is seen that the traps'
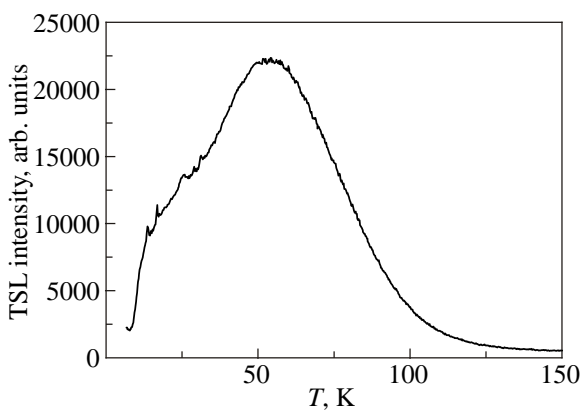
activation energies form five horizontal shelves for the PDHS films on the metal substrate are (0.017 ± 0.0003), (0.026 ± 0.0002), (0.043 ± 0.0003), (0.048 ± 0.0005) and (0.061 ± 0.0005) eV. Raman spectrum of the PDHS film [16] is presented at Fig. 5 (curve *1*). Comparison of the data obtained in the study of the TSL and Raman spectra has shown that the activation energies of the traps correlate well with the frequencies of Si–Si vibrations of the polymer chain: 148 cm^{-1} (0.0183 eV), 214 cm^{-1} (0.0265 eV), 337 cm^{-1} (0.0418 eV), 373 cm^{-1} (0.0462 eV) and 493 cm^{-1} (0.0611 eV), respectively.

Thus, TSL study of PDHS polymer film has shown the presence of additional features on the TSL curves [17] (Fig. 3) which was predicted by the model presented in [18], and the practical coincidence of activation energies of
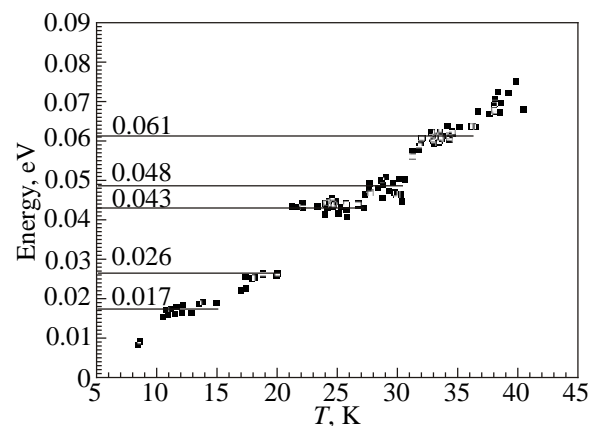

Fig. 3. TSL curve of the PDHS film on a metal substrate.

Fig. 4. Activation energies of the traps determined from the fractional TSL for the PDHS film on a metal substrate. The numbers on the horizontal shelves indicate the activation energies in eV.
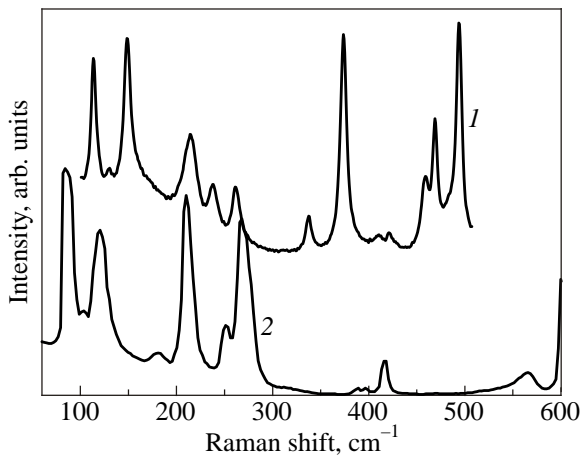
Fig. 5. Raman spectra of PDHS (*1*) [16] and PDHGe (*2*) [10] films at 300 K.

the charge detrapping with the energies of optical vibration modes. These results allow us to conclude that although the energy spectrum of the traps is quasi-continuous, the release of the holes in the polymer is more probable from those traps the depths of which correspond to the energy of Si–Si vibration of the polymer chain.

Figure 6 (solid line) shows the integral TSL curves of the PDHGe film on a metal substrate. We see from Fig. 6 that the TSL curve of PDHGe film is much wider than that of PDHS film (Fig. 3) indicating a larger number of segments (and hence, traps) of different lengths and, accordingly, of different energy. Note that on the TSL curve of the PDHGe film there is no additional structure that is observed on the TSL curve of the PDHS film. In addition to the processes of disordering, this is due to the fact that the TSL intensity of the PDHGe polymer is significantly less than that of the PDHS.

A significant change in the TSL curve is also observed when the polymer is introduced into the SBA-15 silica nanopores. Figure 6 (dotted line) shows the normalized TSL curve of the PDHGe/SBA-15 nanocomposite where
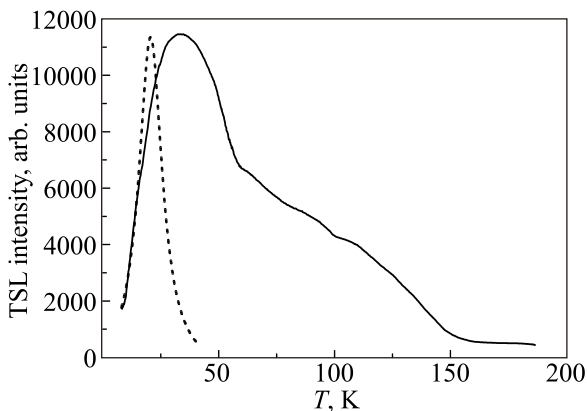
the polymer is introduced into the pores with diameter of 6 nm. From Fig. 6 we see that the curve of the nanocomposite is shifted towards low temperatures by 14 K relative to that of the film. This is associated with decrease in the number of polymer chains in the pore and, subsequently, in the number of traps for charge carriers and decrease in their energy spread. Similar changes in the TSL curve of the PDHS film are also observed when the polymer is introduced into the SBA-15 silica nanopore [22].

Figure 7 shows the activation energies of charge carrier detrapping processes for the PDHGe film measured in the 9–50 K temperature range. The numbers on the horizontal shelves indicate the activation energies in eV. We see that the traps' activation energies form only three discrete levels for the PDHGe films on a metal substrate: (0.0122 ± 0.0005), (0.0308 ± 0.0002), (0.0399 ± 0.0006) eV. Comparison of the data obtained in the study of the TSL and Raman spectrum (Fig. 5, curve *2*) [10] showed that the activation energies of the traps correlated well with the frequencies of Ge–Ge vibrations of the polymer chain: 89 cm^{-1} (0.011 eV), 249 cm^{-1} (0.0309 eV) and 321 cm^{-1} (0.0398 eV), respectively. Comparison of the Raman spectra of the PDHS and PDHGe films (Fig. 5, curves *1* and *2*), respectively, showed that the half-widths of the bands in the Raman spectrum of PDHGe are twice as wide as in the PDHS spectrum, which further confirms the disordering of the PDHGe polymer as compared to the PDHS. As expected for the more disordered PDHGe film, we observe decrease in the number of discrete levels of activation energy for charge carriers (Fig. 7) in comparison with the corresponding levels for the PDHS film (Fig. 4).

So, the heterogeneity leads to the broadening of vibrational bands and causes reduction of the number of observed discrete levels of the traps' activation energy of PDHGe. The manifestation of optical vibrations is more pronounced in the TSL of ordered polymers, in which the vibration bands are narrow.
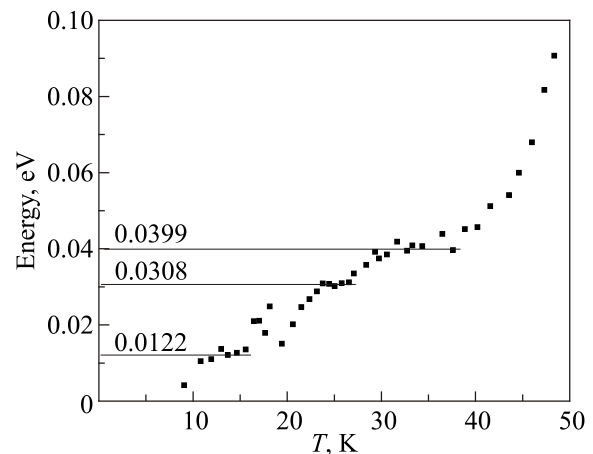

Fig. 6. Normalized TSL curve of PDHGe film (solid line) and TSL curve of nanocomposite PDHGe/SBA-15 (dotted line).

Fig. 7. Activation energies of the traps determined from the fractional TSL for the PDHGe film on a metal substrate. The numbers on the horizontal shelves indicate the activation energies in eV.

Conclusion

Manifestation of polymer chains disordering in the optical spectra, TSL curves and temperature dependence of the activation energy of charge carriers is investigated. The well-studied "crystalline" PDHS polymer and the more disordered PDHGe polymer are considered for comparison. We have shown that the number of bands in the optical spectra of the PDHGe polymer films increases due to the presence of polymer chains with different set of trans- and gauche-conformations. Decrease of the intermolecular interaction between the segments of the polymer chains and increase of their mobility both lead to the change in the conformation of the PDHGe polymer chains introduced into the nanopores of the SBA-15 silica. It changes from the trans-conformation as in the case of PDHS to the gauche-conformation. The disordering effects are associated with the two times broadening of the vibrational bands in the Raman spectra of PDHG as compared to PDHS. Moreover, according to the fractional TSL data, the disordering effects lead to the decrease in the number of discrete activation energies of charge carriers, which appear during resonant absorption of Ge–Ge optical vibration quanta by carriers during their release.

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Вплив упорядкування полімерів на оптичні спектри і термолюмінесценцію полігерманієвих і полісіланових плівок та нанокомпозитів

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Проведено порівняльні дослідження оптичних спектрів та термолюмінесценції плівок і нанокомпозитів полі(дигексил-германія) (ПДГГ) та полі(дигексилсилана) (ПДГС) з різним ступенем впорядкування в області температур 5–200 К. ПДГГ в порівнянні з ПДГС є більш розупорядкованим полімером, що проявляється в появі додаткових смуг в оптичних спектрах, які пов'язані з різним набором транс- та гош-конформацій полімерних ланцюгів, а також в уширенні коливальних смуг в КР спектрах. Розупорядкування ПДГГ призводить до зменшення міжмолекулярної взаимодії між сегментами полімерних ланцюгів та до збільшення їх рухливості, тому полімерні ланцюги, введенні в нанопори кремнезему СБА-15, мають гош-конформацію на відміну від транс-конформації для впорядкованого ПДГС. Дослідження термолюмінесценції показало, що для обох полімерів характерна поява дискретних енергій активації для носіїв заряду, енергії яких співпадають з квантами оптичних коливань.

Число дискретних енергій активації для ПДГГ зменшується, що пов'язано з ефектами його розупорядкування.

Ключові слова: політалани, плівки, нанокомпозити, енергії активації, пастки, термолюмінесценція.

Влияние упорядочения полимеров на оптические спектры и термолюминесценцию полигерманиевых и полисилановых пленок и нанокомпозитов

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Проведены сравнительные исследования оптических спектров и термолюминесценции пленок и нанокомпозитов поли(дигексилгермания) (ПДГГ) и поли(дигексилсилана) (ПДГС) с различной степенью упорядочения в области температур 5–200 К. ПДГГ является более разупорядоченным полимером по сравнению с ПДГС, что проявляется в появлении дополнительных полос в оптических спектрах, которые связаны с различным набором транс- и гош-конформаций полимерной цепи, а также в уширении колебательных полос в КР спектрах. Разупорядочение ПДГГ приводит к уменьшению межмолекулярного взаимодействия между сегментами полимерных цепей и увеличению их подвижности, поэтому его полимерные цепи, введенные в нанопоры кремнезема СБА-15, имеют гош-конформацию в отличие от ПДГС, которые имеют транс-конформацию. Исследование термолюминесценции показало, что для обоих полимеров характерно появление дискретных энергий активации для носителей заряда, энергии которых совпадают с квантами оптических колебаний. Число дискретных энергий активации для ПДГГ уменьшается, что связано с эффектами его разупорядочения.

Ключевые слова: полиметалланы, пленки, нанокомпозиты, энергии активации, ловушки, термолюминесценция.