Carrier Trapping Centers in Polysilane Film

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Abstract

Anomalous behavior of trapping and release of charge carriers in poly(methylphenylsilane) films has been discovered by thermally stimulated current spectroscopy. The carrier trapping occurs effectively at room temperature but not at 77 K. Trapped carriers are released at some specific temperatures which do not depend on the heating rate in the measurements. No trapped carrier is released at room temperature. Differential scanning calorimetry indicates that the onset temperatures of the carrier release correspond to the endothermic peaks. Such carrier trapping and release are not observed for polysilanes with saturated hydrocarbon side group but with aromatic side group. Theses results suggest that the observed phenomena are related to the motion of the aromatic substituents.

Keywords

Polysilane, Carrier trapping, Carrier release, Structural trap

Introduction

Polysilanes have attracted much attention as imaging materials with high hole drift-mobility[1,2] and high efficiency of ultraviolet light emission.[3] A pulse-radiolysis time-resolved-microwave-conductivity measurement has exhibited a carrier drift mobility higher than 10^{-1} cm^2/Vs in polysilane molecules.[1] Unfortunately it has been unknown which carrier of electrons or holes can respond. Recently, a possibility of 0.1 - 1 cm^2/Vs for holes has been pointed out for oriented polysilane films.[2]

The polysilane of poly(methylphenylsilane) (PMPS) shows the photoconduction of which the spectrum has the 0.1 eV higher onset than the optical absorption edge.[4,5] It has been considered that the photocarriers are photogenerated free-holes in a disorder system rather than photogenerated charged-polarons. The temperature dependence of photoconductivity in PMPS films has also been explained by a disorder model. In the related experiments we have found an anomalous temperature dependence of the dark conductivity after exposure to light. In this paper, we report this phenomenon and explore its kinetics by means of thermally stimulated current (TSC) spectroscopy and differential scanning calorimetry (DSC).

Experiment

Polysilanes used were PMPS and poly(methyltoryl-silane) (PMTS) as ones with aromatic side group and poly(cyclohexylmethylsilane) (PHMS) and poly(dipentylsilane) (PDPS) as ones with saturated hydrocarbon side group. These polysilanes were synthesized by condensation of corresponding diorganodichlorosilanes with sodium metal in reflux toluene at about 110 °C in the usual manner. Their molecular weights determined by gel permeation chromatography using polystyrene for calibration were 130,000, 71,000, 120000 and 187,000, respectively.

About 2 µm thick polysilane films were cast on Corning 7059 glass plates or quartz plates. For the electric current measurement the coplanar electrodes of Al with a gap of 100 µm were formed on the polysilane films and samples were kept in a temperature controlled cryostat.

For PMPS sample, thermally stimulated current (TSC) spectra were measured under the electric field of 10^4 V/cm according to a sequence illustrated in Fig. 1. The heating rate was 1.0 K/min. In order to fill traps with carriers, photocarriers were generated for a few seconds by exposure to 350 nm light with 0.45 mW/cm^2 from a Xenon lamp. This excitation energy, which is lower the optical absorption peak energy due to σ–σ* transition but high enough for photocarrier generation, was chosen to avoid the photoinduced creation of defects in the polysilanes.

PMPS sample was cooled down to 77 K after exposure to excitation light at room temperature and then the TSC
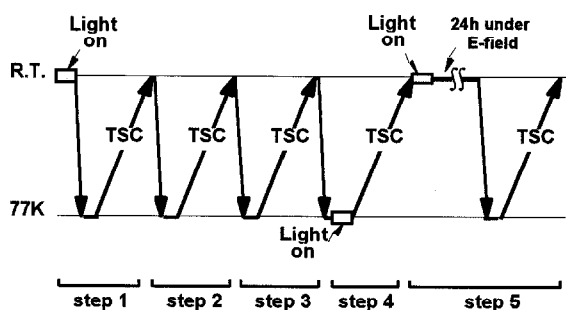
Figure 1. Sequence of TSC measurements for PMPS

spectrum was measured up to 300 K. This is step 1. In step 2 this sample was cooled down again to 77 K without exposure to excitation light and the TSC spectrum up to 300 K was measured. This procedure was repeated for step 3. Then the sample was cooled down and the TSC spectrum up to 300 K was measured after exposure to excitation light at 77 K for step 4. In step 5 the TSC spectrum was measured after the sample was exposed to excitation light and stored under the electric field of 10^4 V/cm in the dark for 24 hours at room temperature.

Similar TSC experiments were performed for other polysilane films, where the excitation energy was adjusted to the respective subgap energies (slightly lower than the absorption peaks due to σ–σ* transition).

The DSC measurement was performed for powder samples when the temperature increased from 200 K to 300 K at the rate of 5.0 K/min. Optical absorption spectra were also measured as a function of the temperature from 200 K to 290 K.

Results

Figure 2 shows the TSC spectra for steps 1 to 5. Step 1 exhibits a main peak at 228 K (peak 1) and a sub peak at 277 K (peak 2). The intensity of peak 1 is 20 times larger than the background. For step 2 these two peaks still appear, although the intensity of peak 1 decreases to 1/3. However, they disappear for step 3. We have confirmed that the positions of the two peaks do not depend on the heating rate.

For step 4 the two peaks clearly appear, but the intensity of peak 1 is quite small. This indicates that the trapping of photocarriers is harder at 77 K than at room temperature. For step 5 peak 1 appears and has almost the same intensity as that in step 1. This peak also appears when no voltage is applied to the sample during the storage in the dark after excitation of photocarriers. It is noted that the thermal energy at room temperature is not enough to release the trapped carriers. This is related to the fact that peak 1

does not disappear even after the experience of room temperature (step 2). When the temperature increased beyond 320 K, the trapped carriers started to be released, which is not shown in Fig. 2.

Discussion

The ordinary analysis[6] of the TSC spectra in Fig. 2 with a frequency factor of 10^{12} s^{-1} gives rise to a single trap level at 0.67 eV for peak 1. However, this is not applicable for the case, because 1) the peak positions in the TSC spectra do not depend on the heating rate, 2) the release rate of the trapped carriers does not obey a simple Arrhenius equation, 3) the trapped carriers are released at specific temperatures, and 4) the trapping of photocarriers is effective at room temperature but not at 77 K. Comparison of the carrier-trapping and release between ordinal semiconductors and PMPS is illustrated in Fig. 3.

One possible origin to cause the observed phenomena is a structural change as a function of temperature. Figure 4 shows the optical absorption spectra at different
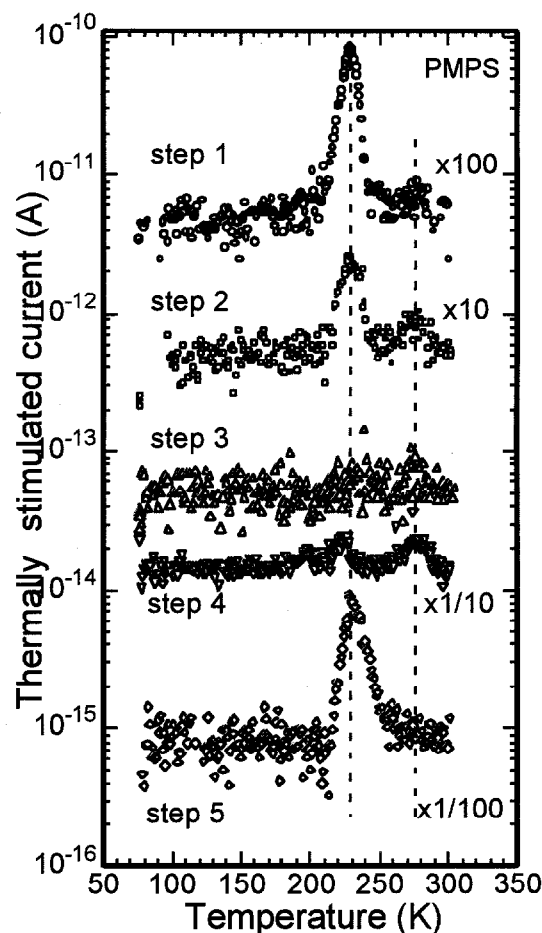

Figure 2. TSC spectra of PMPS measured according to the sequence in Fig.1.
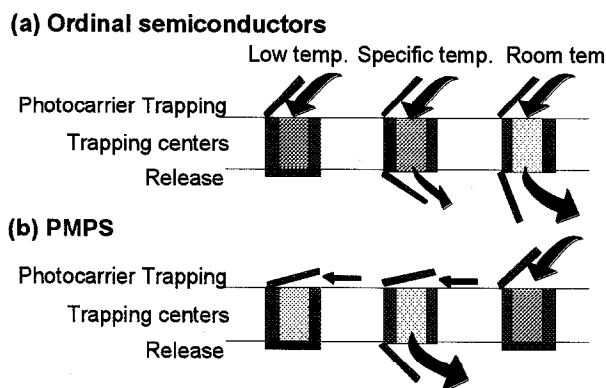
(a) Ordinal semiconductors

Low temp. Specific temp. Room tem

Photocarrier Trapping

Trapping centers

Release

(b) PMPS

Photocarrier Trapping

Trapping centers

Release

Figure 3. Comparison of the carrier trapping and release between (a) usual semiconductors and (b) PMPS.

more detail, we performed the DSC measurement. Figure 5 shows the DSC spectrum for PMPS powder. Three weak dips are observed in the spectrum. The derivative of the heat flow with respect to the temperature clearly exhibits that endothermic reactions occur at 206 K, 237 K and 266 K. The two peaks of the three, at 206 K and 266 K, correspond to the onsets of peaks 1 and 2 in the TSC spectra shown in Fig. 2, respectively. This correspondence is obviously seen in Fig. 5 where the spectrum of step 1 is replotted. Since sample used in the DSC measurement was not a film but powder, this result indicates that the release of trapped carriers is related to some structural change associated with the nature of the polysilane. In other words, the TSC measurement is a sensitive tool to detect this kind of structural change.

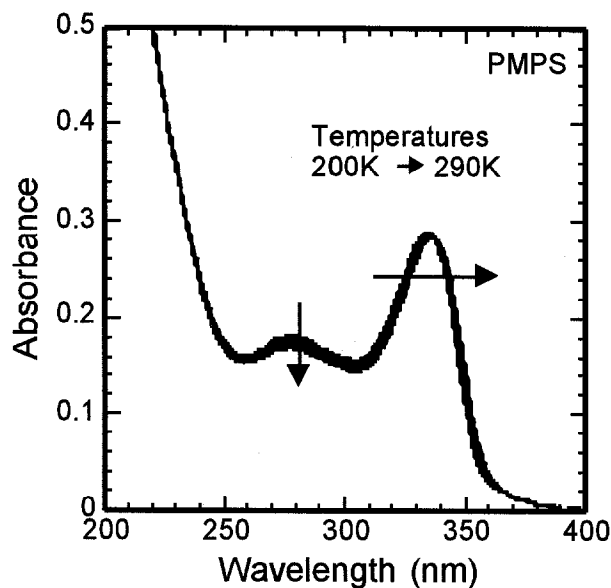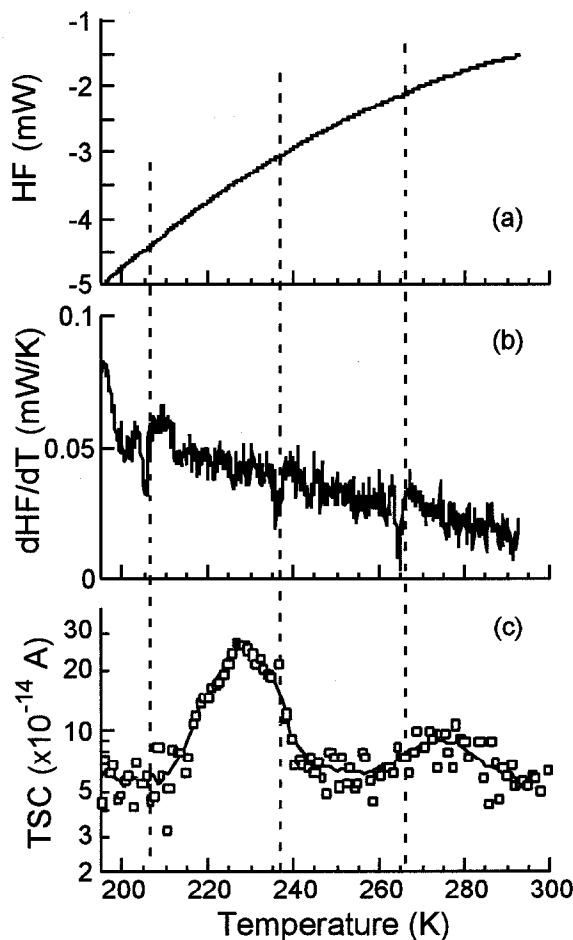The TSC measurements have been performed for other polysilanes such as PMTS, PHMS and PDPS. Only PMTS,

Figure 4. Temperature dependence of optical absorption spectra of PMPS.

temperatures between 200 K and 290 K. Peaks around 336 nm and 278 nm are due to the σ–σ^* transition in the amorphous state of Si backbone and the π–π^* transition in phenyl substituents, respectively. With increasing the temperature the peak around 336 nm redshifts and the intensity of the peak around 278 nm decreases. However, these changes are quite small and continuous. Thus PMPS does not show considerable thermochromism at specific temperatures, as is well known,.

In order to explore the structural change of PMPS in

Figure 5. (a) DSC (heat flow) spectrum of PMPS powder, (b) differential coefficient of DSC curve, and (c) TSC spectrum of step 1 in Fig.2.

which has aromatic substituents, shows behaviors similar to PMPS. The peaks appear at 212 K, 233 K and 270 K. These results lead us to have a consideration that the events of the carrier trapping and release are related to the motion of the aromatic sbustituents. What happens with the aromatic substituents? A hypothetical model to answer the question is as follows. When their distance is quite small, the two aromatic substituents have a strong interaction to form a π–π state which is a trapping center for a hole. Its energy level is so deep that a trapped carrier cannot be released even at room temperature. The π–π state would be formed to trap a hole only when the hole reaches near a pair of aromatic substituents which are close each other. Thus some of photogeneareted holes migrate to find such trapping centers, while photogenerated electrons are localized in the Si backbones and cannot recombine with the trapped hole. The process forming the π–π state with a hole requires the motion of the morecules and consequently proceeds at room temperature rather than at 77 K. Furthermore, the hole trapped π–π states are broken and trapped holes are released when endothermic reactions, i.e. the motion of aromatic substituents occur. This point needs further clarification.

Conclusion

TSC measurements revealed that the polysilanes with aromatic side group show the anormarous temperature dependence of the carrier trapping and release. The carrier trapping is effective at room temperature but not at 77 K. The trapped carriers are released at specific temperatures which do not depend on the heating rate in the measurements. A hypothetical model has been proposed, in which the hole trapping is caused by forming π–π states and the hole trapped π–π states are broken to release the trapped holes by the motion of aromatic substituents as the endothermic reaction.

Acknowledgements

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Biography

Yoshikazu Nakayama received his B.S. degree in Electric Engineering from Osaka Prefecture University in 1972, and a Ph.D. in Applied Physics from Osaka University in 1985. In 1972, he joined Matsushita Electric Industry Co., Ltd. where he worked on research in optical memory using holograms. In 1979, he moved to Osaka Prefecture University and have worked on solid-state physics, especially photoconductive materials, and plasma processing for semiconductor materials. He was appointed to the position of professor in 1995.