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CHARGE HOPPING TRANSPORT STUDIES IN Σ-CONJUGATED POLYSILANES

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Abstract Thermally Stimulated Current (TSC) and Time Of Flight (TOF) measurements were performed on polymethylphenylsilane (PMPS) to study the mechanism of interchain hole hopping transport in these materials. In TSC spectra a well defined current peak was observed between 100K-150K. The peak temperature was dependent on applied electric field and heating rate. The corresponding activation energy ranged between 0.20eV at 30V/μm to 0.33eV at 5V/μm, as obtained by both TSC and TOF spectroscopies. Photogeneration at 80K was studied as a function of illumination energy and electric field. For samples irradiated by more than ~1mJ, a secondary peak at ~180K was observed in TSC. The secondary peak, with corresponding activation energy of 0.5eV, was associated with trapping states induced by the UV defect sites. The filling fraction of those states was dependent both on illumination energy and electric field.

INTRODUCTION

Polysilanes are photoactive materials[1], consisting of σ-conjugated Si atoms along the polymer backbone, and two organic side groups pendant on each Si atom. Their novel electronic structure[2-4] results in photoactivity in the near UV[5-8], leading to applications as photoresists[9,10], and also to high hole conductivity[11-13]. We report charge transport studies aimed at understanding the nature of the interchain hopping transport in these materials. Measurements of a modified version of thermally stimulated current (TSC) and time of flight (TOF) spectroscopy were performed on poly(methylphenylsilane). Both methods monitor the transport of the charge through the sample, after photogeneration near the surface by UV radiation and separation by the assistance of the applied electric field. While in TOF measurements the transient transport of the charge is probed in situ, the TSC technique delineates hopping states associated with different activation energies. The combined results from these complementary methods lead us to a better understanding of the mechanism of charge hopping transport in these materials.

EXPERIMENTAL

The PMPS polymer was prepared by condensation of a purified organosilicon dichloride monomer with sodium dispersion, using the inverse addition method.

End capping was activated using chlorodimethylphenylsilane. The details of the synthesis are discussed in Ref.14. The samples, which were 4-5μm thick, were cast from the polymer solution in toluene (6.5% weight ratio), and were coated onto an Aluminum Mylar substrate, which served as the bottom electrode. The top Al electrode, which was vapor deposited, was semitransparent in the UV and blocking for hole injection. Electric field was induced by applying positive voltage onto the top electrode. In TSC measurements, the sample was illuminated by a pulsed Nitrogen laser (337nm) at 80K and under an applied electric field. Illumination energy was controlled by neutral density filters and by the number of the laser pulses. After illumination, the sample's temperature was ramped linearly in time while the sample was in the dark under an electric field. The current was measured by an electrometer in series. The electric field was varied between 5V/μm to 30V/μm, and the illumination energy was varied between 0.05mJ to 2.5mJ.

TOF measurements were performed on the same samples, using the conventional procedures.

RESULTS AND DISCUSSION

Upon illumination, generation of charge carriers occurs at the top surface region (~500Å)[11] by the field assisted dissociation of the photoexcited electron-hole pairs. The charge carriers, which are known to be holes[11], are frozen into the hopping states at 80K. When the sample's temperature is ramped, their mobility increases exponentially, leading to the observed increase in the current. The decrease in the current at higher temperatures is due to the depletion of those charge carriers. The overall spectrum consists of a single current peak at temperature T_m, which shifts to higher temperature with increasing heating rate under a constant electric field. In contrast, for a constant heating rate the peak temperature decreases with electric field.

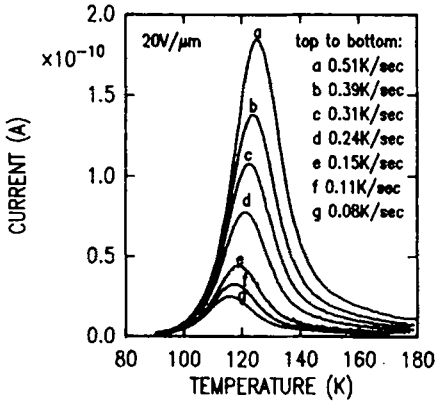

FIGURE 1. TSC spectra at 20V/μm and various heating rates.

Fig.1 shows some TSC spectra for measurements performed at a constant electric field of 20V/μm and heating rates ranging between 0.08K/sec to 0.51K/sec. The activation energy associated with the interchain hopping trans-

port was derived from the peak temperature shift with heating rate, according to:[15]

$$\ln(R/T_m^2) = -E_a/kT_m$$

where R is the heating rate, T_m is the peak temperature, E_a is the activation energy and k is Boltzmann constant.

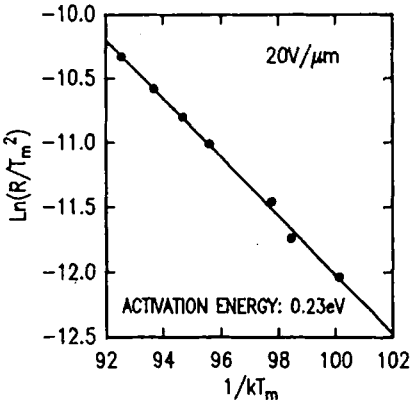

FIGURE 2. Ln (R/T_m^2) vs. $1/kT_m$ at 20V/μm.

Fig. 2 shows the plot of ln (R/T_m^2) vs. $1/kT_m$ for an electric field of 20V/μm. The slope of the line fitted to the curve yields the activation energy at that field. The values of the activation energy, ranged between 0.20eV at 30V/μm to 0.33eV at 5V/μm, and were consistent with those obtained from TOF experiments performed on the same samples.

The amount of charge photogenerated at 80K, calculated from the time based TSC curves, ranged between $1x10^{-9}$ to $4x10^{-8}$C. It varied both with illumination energy and electric field. It was, however, independent of the heating rate. These results suggest that geminate recombination plays a role in determining the amount of photogenerated charge in the generation region, but no recombination occurs at the bulk during the charge transport through the medium. These assumptions are supported also by the fitting of the experimental results to a model, which considers recombination of electron-hole pairs only at the top generation layer during the TSC experiment[16].

Fig.3 shows the dependence of the photogenerated charge on illumination energy for electric fields of 10, 20 and 30V/μm. The amount of charge generated in TOF experiments, performed at room temperature, ranged between $5x10^{-10}$ to $7x10^{-9}$C per single laser pulse, and was also dependent both on electric field and the illumination energy. The consistency of the results from both methods supports the applicability of the modified version of TSC spectroscopy to study charge hopping transport through the bulk, in distinction from the conventional TSC method, which is commonly used for "trap" spectroscopy[17].

For samples which were irradiated by ~1mJ, a secondary peak at ~180K was observed. The intensity and the structure of that peak were dependent both on electric field and illumination energy. The peak temperature increased with heating rate, yielding an activation energy of 0.5eV. However, the peak temperature

and the corresponding activation energy were independent of the electric field, unlike the main peak.

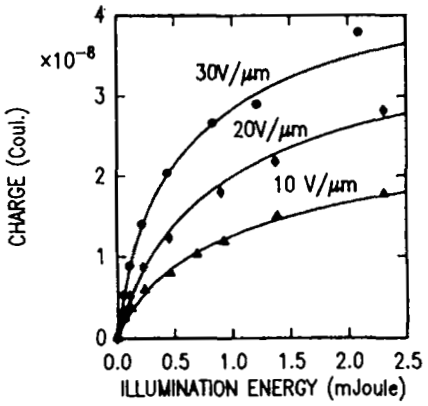

FIGURE 3. Photogenerated charge vs. illumination energy at various electric fields.

Fig.4 shows several TSC spectra measured at an electric field of 20V/μm and illumination energy ranging between 0.05mJ to 2.3mJ.

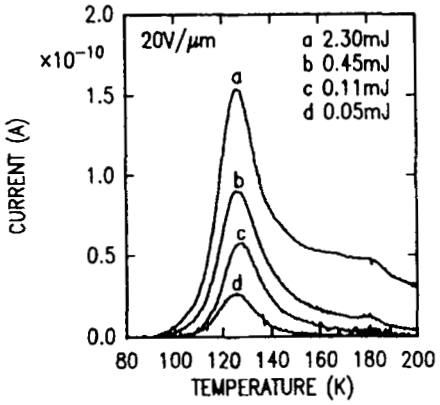

FIGURE 4. Filling of photodegradation-induced traps at 20V/μm and various illumination energies.

Fig.5 shows TSC curves for 2.3mJ illumination energy and electric fields of 10, 20 and 30V/μm. The dependence of the peak structure and intensity on illumination energy suggests that the secondary peak is associated with surface defect sites produced by the UV radiation. The photodegradation of the sample is also manifested by the gradual decrease in the charge photogeneration efficiency. Breaking of Si-Si bonds in the polymer backbone, which has been observed in ESR measurements[18], may account for these effects, as well as for the photogenerated impurities observed by luminescence spectroscopy in solid solution of PMPS[19].

The trapping states associated with these sites are occupied by excess charge, after the bulk hopping states have been populated on illumination at 80K. The filling fraction of the traps increased with illumination energy under a constant electric field, and decreased with electric field for a constant illumination energy. When the samples were irradiated at higher doses, the amount of trapped charge increased significantly and became comparable to the untrapped charge that transfered through the bulk. The structure of the peak also became less defined and appeared as a broad shoulder on the high temperature side of the main peak.

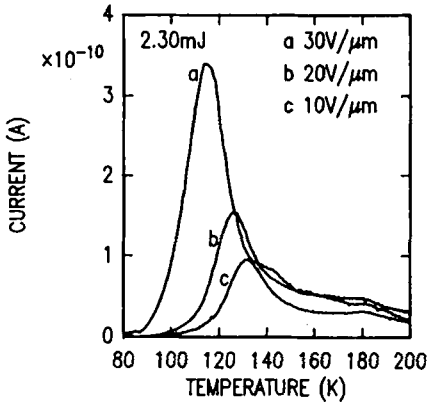

FIGURE 5. Filling of photodegradation-induced traps at 2.30mJ and various electric fields.

In summary, charge hopping transport in PMPS has been probed, using TSC and TOF spectroscopies. The activation energy correlated with the process ranged between 0.20eV at 30V/μm to 0.33eV at 5V/μm. The amount of photogenerated charge was dependent both on illumination energy and electric field. The filling fraction of the trapping states apparantly introduced induced by the UV damage was also dependent on those factors.

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