Original paper

Substituent Dependence and Orientation Effect on Carrier Trapping in Polysilane Films

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Abstract Thermally stimulated current measurements for polysilanes with aromatic substituents have been performed to investigate the behavior of trapping and release of charge carriers. Different kinds of the substituents (phenyl, p-tolyl and m-tolyl) with and without the orientation of the main chains are examined. It is found that the trapped carriers are released at some specific temperatures exhibiting the endothermic motion of polysilanes but cannot be released completely in one scan of the measurement. This behavior has been analyzed by introducing a concept of the temperature-dependent lifetime of trapped carriers. It is considered that the aromatic substituents in polysilanes form $\pi-\pi$ states to be trapping centers for holes and the trapped holes are released by the endothermic motions of the substituents. The analysis reveals that 1) the substituents examined have two principal hole-release peaks at 215K–219K and 226K–234K, 2) the orientation broadens the peak widths, and 3) the orientation also shifts the peaks to higher temperatures for polysilanes with phenyl and p-tolyl but not for polysilanes with m-tolyl because of its strong steric hindrance.

Key words: polysilane, carrier trapping, aromatic substituent, orientation, steric hindrance

1. Introduction

Organic semiconductors have been widely used as imaging materials. Polysilanes show remarkable properties such as photoconductivity and high carrier mobility, which are expected to be used as the high mobility carrier transport materials [1][2]. We have reported the anisotropy of photoconduction for the oriented polysilane films which were prepared by an electric field induced method [3][4] and an air-flow dipping method [5][6]. The photoconduction is one order of magnitude higher along the Si chains and two orders of magnitude less perpendicular to the Si chains than for unoriented films. We have also developed a method to stretch polysilanes along the film thickness by SAT. Carrier trapping was measured by a TSC technique. For the electric current measurement, Al coplanar electrodes with a gap of 100 µm were formed on the oriented polysilane films and the samples were kept in a temperature-controlled cryostat. TSC spectra were measured under the relatively low electric field of $10^4$V/cm. The heating rate was 2.0K/min. In order to fill traps with carriers, photocarriers were generated by exposure to 354nm light with 0.45mW/cm² from a Xe lamp for 3s. This excitation energy, which is lower than the optical absorption peak energy due to $\pi-\pi^*$ transition but high enough for photocarrier generation, was chosen to avoid the photoinduced creation of

2. Experimental

Polysilanes used were poly(methylphenylsilane) (PMPS), poly(methyl-p-tolylsilane) (p-PMTS) and poly(methyl-m-tolylsilane) (m-PMTS) with molecular weights of 30,800 and 13,000 and 35,700, respectively. Their molecular formulas are shown in Fig. 1. Polysilanes were spin-casted or simply casted on substrates to form films. The film was sandwiched with a spacer and a cover glass plate and oriented along its thickness by SAT. Carrier trapping was measured by a TSC technique. For the electric current measurement, the coplanar electrodes of Al with a gap of 100µm were formed on the oriented polysilane films and the samples were kept in a temperature-controlled cryostat. TSC spectra were measured under the relatively low electric field of $10^4$V/cm. The heating rate was 2.0K/min. In order to fill traps with carriers, photocarriers were generated by exposure to 354nm light with 0.45mW/cm² from a Xe lamp for 3s. This excitation energy, which is lower than the optical absorption peak energy due to $\sigma-\sigma^*$ transition but high enough for photocarrier generation, was chosen to avoid the photoinduced creation of

![Fig. 1 Three kinds of polysilanes with aromatic substituents used in this experiment.](image-url)
Fig. 2 Experimental procedure of TSC measurements.

Fig. 3 TSC spectra of the oriented (open circle) and unoriented (closed circle) films of PMPS measured according to the procedure in Fig. 2.

defects in the polysilanes. Sample was cooled down to 77K after exposure to excitation light at room temperature and then the TSC spectrum was measured up to 300K. This procedure was repeated until spectrum was disappeared, as show in Fig. 2.

3. Results

Figure 3 shows the TSC spectra of the oriented and unoriented films of PMPS for the 1st to 4th runs. In case of the 1st run, the unoriented film exhibits a main peak at 221 K and a sub peak at 245 K. Due to the orientation, the main peak shifts to 225 K and becomes broadened. For the 3rd run these two peaks still appear, although the intensity of the peaks decreases. However, they almost disappear for the 4th run. These trapped carriers are not released during the storage of the sample in the dark at room temperature after filled by excitation. 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 the peaks do not disappear even after the experience of room temperature.

Figure 4 (a) shows the differential coefficient of DSC curve for PMPS powder and (b) shows again the TSC spectra of 3rd run for the unoriented PMPS film shown in Fig. 3. The derivative of the heat flow with respect to the temperature clearly exhibits that endothermic reactions occur at 214K and 244K. The two peaks correspond to the two peaks in the TSC spectra shown in Fig. 4 (b), respectively. This result indicates that the release of trapped carriers is related to some structural changes associated with the nature of the polysilanes.

4. Theoretical Analysis and Discussions

The anomalous behavior of the carrier trapping in polysilanes can not be explained by the conventional formalism used for the analysis of carrier trapping in normal semiconductors, because the carriers can not be released completely after one scan. It is necessary to establish a new formalism to interpret such phenomena. It is well known that holes are the main free carriers for transport in the conjugated polysilanes. Thus, we assume that the trapped carriers are holes. These trapped holes do not vanish until after several times scan in the TSC measurement. From the results of DSC, the release of trapped holes happens only in some specific temperatures where the endothermic reactions occur. According to these results mentioned above, We assume that the trapped holes have a temperature-dependent lifetime $\tau$, which is corresponding to the time constant of the endothermic reaction. The amount of holes released at temperature $T$ is described as

$$N(T) = N_0(T) \left[ 1 - \exp \left( -\frac{\Delta t}{\tau} \right) \right],$$

(1)

where $N_0(T)$ is the amount of resident trapped holes at a temperature $T$ and $\Delta t$ is the decay time. We assume that $\tau$ has a Gaussian distribution described as

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \frac{1}{\frac{1}{\tau_0} + \frac{1}{\Delta t}} \exp \left[ -\frac{(\alpha t - T_{\text{max}})^2}{2\sigma^2} \right],$$

(2)

in which $T_{\text{max}}$ and $\sigma$ are the peak temperature and the width of the distribution, respectively. $\alpha$ is the heating rate and $t$ is the measurement time. The TSC spectra for the oriented and unoriented PMPS films are reconstructed using Eqs. (1) and (2) with suitable $T_{\text{max}}, \sigma$ and $\tau$. The result is shown in Fig. 5. The experimental data are indicated by the open circles and calculated data are indicated by the solid lines. Each spectrum consists of three peaks which are shown by dashed lines and are named peak 1, peak 2 and peak 3. The TSC spectra are well fitted by the calculated curves and the fitting parameters are listed in Table 1. Due to the orientation, the main peak shifts to a higher temperature and the $\tau$ value decreases, i.e. the release rate increases. The
values of $T_{\text{max}}$ for peak 1 and peak 3 are almost the same as those of the DSC peaks, indicating that the release of the holes is related to the endothermic reactions. However there is no clear peak in the DSC spectrum for PMPS powder corresponding to the $T_{\text{max}}$ value for peak 2. It is also found that the $\tau$ for peak 2 is quite smaller than the other ones, relating to a quick decay of the peak. It is noted that peak 2 is present for the film but not present in the DSC spectra for the powder. This result suggests that the endothermic motion at 226K–234K appears only for films.

Based on the overall results and analysis, we propose a model of carrier trapping and release for PMPS, which is illustrated in Fig. 6. In PMPS, the adjacent two aromatic substituents that are close to each other have a strong interaction to form a $\pi-\pi$ state which acts as a trapping center for a hole. Its energy level is so deep that a trapped hole cannot be released at room temperature. It has been reported that this hole starts to be released when the temperature is raised beyond 320 K\(^{10}\). The hole-trapping $\pi-\pi$ states are broken and the trapped holes are released when the endothermic reactions, i.e. the motions of the aromatic substituents occurs at temperatures lower than room temperature.

When the aromatic substituents can easily separate, the trapped hole has a small $\tau$. When the aromatic substituents close to each other, the interaction becomes stronger to form a deeper trapping center, the trapped hole would have a larger $\tau$.

The same behaviors have also been observed for $p$-PMTS and $m$-PMTS. Figure 7 shows the TSC spectra for $p$-PMTS films (a) without and (b) with orientation and the spectra for $m$-PMTS films (c) without and (d) with orientation. The separated peaks calculated by Eqs. (1) and (2) with suitable $T_{\text{max}}$, $\sigma$ and $\tau$ for each spectrum are also plotted. The fitting parameters are listed in Table 1. It is found that two principle peaks at 215K–219K and 226K–234K are present in all the three kinds of polysilane films with and without orientation. Due to orientation, $p$-PMTS shows that the two peaks are shifted from 215K and 226K to 219K and 234K and their values of $\tau$ are decreased, which are the same as those of the peak 2 in PMPS as shown in Fig. 5. It is noted that a new small peak appears at the lower temperature of 206 K for the unoriented $p$-PMTS film (207K for the oriented film). This peak is not observed in the TSC spectra for PMPS, and the corresponding peak does not appear in the DSC spectra for $p$-PMTS powder, suggesting that this is a unique peak for the film. This is considered to be mainly contributed to the larger interactions among the polysilane molecules in film than in powder. Furthermore, the higher temperature peak at 245K comparable to the peak 3 in PMPS only appears in the oriented $p$-PMTS film. The reasons for these results are not known clearly, but it is clear that the endothermic reaction temperatures for powder are different from those for film and are affected by the kinds of substituents and the orientation of the polysilane films. The packing and interactions among the main chains or the substituents may be the important factor resulting in the different carrier-trapping behavior in powder and film. This is a valuable subject for our further studies. For $m$-PMTS, however, the orientation almost does not change the TSC peaks corresponding to those in the unoriented film, suggesting that the steric hindrance of the $m$-tolyl groups is larger than that of the phenyl or $p$-tolyl groups to make their motions difficult so as not to be sensitive to the orientation. This result is consistent with a reasonable consideration that the addition of methyl to a phenyl ring at the asymmetric meta position would limit the motion of the substituent, for example, the rotation of the phenyl ring. Like $p$-PMTS, two new peaks around

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**Table 1** Fitting parameters for TSC spectra of 1st run for the oriented and unoriented films of PMPS, $p$-PMTS and $m$-PMTS.

<table>
<thead>
<tr>
<th>Polysilane film</th>
<th>Unoriented $T_{\text{max}}$ (K)</th>
<th>$\sigma$ (k)</th>
<th>$\tau$ (s)</th>
<th>Oriented $T_{\text{max}}$ (K)</th>
<th>$\sigma$ (k)</th>
<th>$\tau$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMPS</td>
<td>216</td>
<td>8.0</td>
<td>37</td>
<td>216</td>
<td>8.0</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>226</td>
<td>5.2</td>
<td>13</td>
<td>232</td>
<td>7.0</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>245</td>
<td>6.0</td>
<td>71</td>
<td>241</td>
<td>6.0</td>
<td>34</td>
</tr>
<tr>
<td>$p$-PMTS</td>
<td>206</td>
<td>4.0</td>
<td>63</td>
<td>207</td>
<td>4.0</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>215</td>
<td>4.0</td>
<td>52</td>
<td>219</td>
<td>6.0</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>226</td>
<td>5.0</td>
<td>12</td>
<td>234</td>
<td>6.5</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>245</td>
<td>6.5</td>
<td>32</td>
</tr>
<tr>
<td>$m$-PMTS</td>
<td>204</td>
<td>5.5</td>
<td>50</td>
<td>217</td>
<td>5.5</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>228</td>
<td>5.0</td>
<td>10</td>
<td>228</td>
<td>5.5</td>
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<td>4.0</td>
<td>70</td>
<td>238</td>
<td>4.5</td>
<td>70</td>
</tr>
</tbody>
</table>
Fig. 7  TSC spectra for p-PMTS films (a) without and (b) with orientation and the spectra for m-PMTS films (c) without and (d) with orientation. The solid circles indicate the experimental data and the dashed lines indicate the calculated curves. The solid line is the composite curve of the separated peaks for each spectrum.

204 K and 232 K appear in the oriented m-PMTS, which is probably due to the deformation and the stress of the tolyl substituents produced in the orientation by the outer force. It is found that the orientation also increases the width of almost all the peaks for the three kinds of polysilane films. This suggests that the oriented polysilanes contains larger stresses raised by the stretching force so that the spatial positions of substituents are fluctuated wider from the energy-minimum position to form the wider ranged trapping levers.

5. Conclusion

Polysilanes with aromatic substituents have the anomalous temperature dependence of the carrier trapping and release. The hole trapping is caused by the π–π states formed by the interaction among the aromatic substituents. These π–π states are broken to release the trapped holes by the motion of aromatic substituents due to the endothermic reaction. The analysis of TSC spectra for PMPS and p-PMTS reveals that the orientation increases the endothermic reaction temperature and lowers the trapping energies. p-PMTS also shows unique behaviors of hole trapping, which is different from PMPS. For m-PMTS, the peak positions and the release rate do not show large changes after orientation, which is discussed to be caused by the steric hindrance of the m-tolyl groups.

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References