Photoconduction in Polysilane Film

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Abstract

The photoconduction of poly(methylphenylsilane) doped with and without C_{60} has been studied in terms of the carrier generation kinetics. The photoconductivity spectrum of polysilane has an onset coincident with the optical absorption edge and this photoconduction is not due to the hole creation from excitons at electrodes but due to photogeneration of holes in the disorder system or photogeneration of charged polarons. The analysis of the disorder model successfully explains the zero temperature photoconductivity. Doping of C_{60} well sensitizes the photoconductivity of polysilane in the spectral region where C_{60} has optical absorption. This sensitization is suppressed at lower temperature. In a low temperature region holes accumulate by the photoexcitation of polysilane and the dark and photoconductivities increase. The accumulated holes recombine with electrons in C_{60} at temperatures higher than 130 K.

Introduction

It is well known that the polysilanes are organic materials with mobility as high as 10^{-4} cm^2/Vs even in unoriented films.[1] It is generally accepted that the carrier is hole and transports by hopping between sites which are segments consisting of 15 ~ 30 Si units separated each other by kinks and/or other conformation defects.[2] The oriented film shows one order of magnitude higher mobility along the orientation and one order of magnitude less mobility perpendicular to the orientation as compared with the unoriented one.[3] A possibility to realize a mobility of the order of 1 cm^2/Vs has been pointed out for the oriented film.[4] This anisotropy is caused by the difference in the hopping distance between the intrachain hopping and interchain hopping.

The polysilane of poly(methylphenylsilane) (PMPS) shows the photoconduction and the doping of C_{60} in PMPS sensitizes the photoconduction.[5, 6] C_{60} incorporated in the polysilane effectively accepts a photogenerated electron to leave a hole in the polymer chain. It has been reported that PMPS shows the photocurrent spectrum with coincidence of onsets for photocurrent and absorption edge.[7] The measurement has been done for a sandwich structure of sample with a transparent electrode through which the PMPS film is exposed to light. This result has been explained by a model where the transparent electrode acts as an acceptor to extract electrons from excitons.[7] However, this explanation is not conclusive.

In this paper, we explore the kinetics of photogeneration of carriers in PMPS films by measuring the photoconduction as a function of the temperature and exciting energy using a sample configuration with coplanar electrodes. We also investigate the case of PMPS films doped with C_{60}.

Experiment

Polysilane of PMPS was synthesized by polymerization of methylphenyldichlorosilane with sodium metal in toluene at about 110 ˚C in the usual manner. The molecular weight was determined to be 130,000 by gel permeation chromatography using polystyrene for calibration. The polysilane films with thickness of 40 µm were formed on Corning 7059 glass plates by a casting technique. The fullerene doped films were also prepared in the same manner using the C_{60}/polysilane mixture solution with the weight ratio of 4%. C_{60} powder used was prepared by dc arc discharge using graphite electrodes and had the purity of at least 90%. Furthermore, the oriented films of PMPS were prepared by mechanically stretching the films peeled off from the substrate. The coplanar electrodes of Al with a gap of 100 µm were formed on the films, and for the oriented film they were prepared to measure the photocurrent along the orientation. A sandwich structure of ITO transparent electrode/ polysilane film (250 nm)/ Al electrode was also prepared for the measurement of electric field dependence of photocurrent.

Photoconductivity measurements were performed with a xenon lamp as a light source for samples kept in a temperature controlled cryostat. The applied electric field was 10^4 V/cm except for the measurement of electric field dependence. The data were taken in a pointwise manner to exclude any distortion due to residual internal space charge accumulation.

Photothermal deflection spectroscopy (PDS)[8] was performed to measure the optical absorption coefficient in the subgap spectral region of the films. The deflection medium used was 1,4 butanediol which does not dissolve polysilane.

Results

Figure 1 shows the spectra of the normalized photoconductivity $\sigma_p/eG=\eta\mu\tau$ and the optical absorption coefficient at room temperature for PMPS films with and

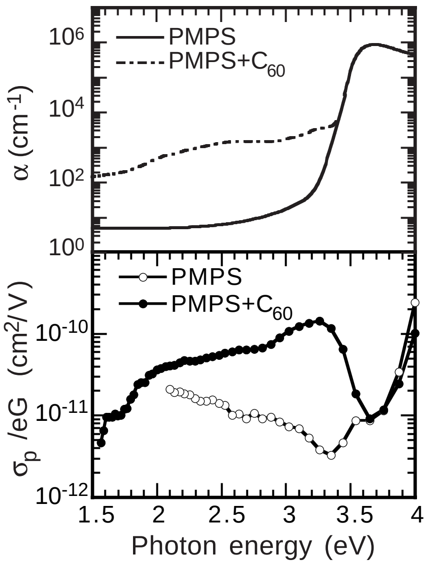

Figure 1. Spectra of optical absorption α and normalized photoconductivity σ_p/eG of PMPS films with and without C_{60}.

without C_{60}. Here G is the excitation rate per cm^3. For the PMPS film, the PDS measurement revealed the sharp band tail with the Urbach energy of 40 meV and quite low absorption coefficients in a low energy spectral region, i. e. low density of states (DOS) in the midgap. The photoconductivity spectrum has two onsets: the low energy onset is corresponding to the absorption edge at ~3.3 eV and the high energy onset is higher than the absorption edge by ~0.4 eV. Even at low photon energies less than the absorption edge, the photocurrent is able to be observed and the calculation gives high σ_p/eG values because of low absorption coefficient less than 10 cm^{-1}.

The doping of C_{60} modified the absorption spectrum of polysilane in a range less than 3.3 eV. It is obvious that the high values of σ_p/eG in the subgap spectral region are well corresponding to the high absorption coefficient caused by C_{60}. The steep increase of the photoconductivity at photon energies higher than 3.7 eV is the same as the variation in the PMPS sample.

Figure 2 shows the temperature dependence of σ_p/eG measured for PMPS films. In this measurement the spectrum ($h\nu$ < 3.8 eV) of xenon lamp with a filter was used. However, the light intensity at $h\nu$ > 3.6 eV is so weak that light with 3.4 ~ 3.6 eV mainly contributes to the photocurrent. The photoconductivity is observed even at a low temperature of T = 15 K and rises steeply at T > 200 K. However, it decreases at T > 240 K. This is because of the photodegradation of the sample. The dotted line is an expected curve.

In the figure the curve for the oriented film of PMPS is also plotted. This measurement was done using rather weak light to avoid the photodegradation of the film and then the data are scattered. The value of σ_p/eG begins to rise at 100 K which is lower than that for the unoriented film.

Figure 3 shows the temperature dependence of dark I_d, photocurrent I_p and σ_p/eG measured for the C_{60} doped PMPS film on 3.54 eV excitation. At 15 K the I_d value is ~ 10^{-14} A which is comparable to the noise level and the I_p value is ten times higher than the I_d value. The values of I_d and I_p, both increase with increasing the temperature up to 130 K. However, this is not a real temperature dependence. We have confirmed that the dark and photocurrent increase to be respective saturated values with time even when the sample is kept at a constant temperature of 77 K. At 130 K the I_d value begins to decrease and becomes the noise level at T > 200 K. On the other hand, the I_p value reaches forty times higher than the I_p value at T > 200 K. The temperature dependence of the photocurrent in this temperature region is not thermally activated.

Discussion

For the photoconductivity spectra in Fig. 1 the free carrier generation at low photon energies less than the absorption edge of PMPS for two samples is not caused via exciton formation. Its origin is impurities and defects for the

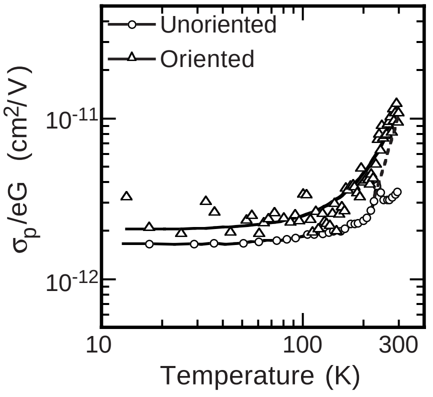

Figure 2. Temperature dependence of normalized photoconductivity σ_p/eG for oriented and unoriented PMPS films.

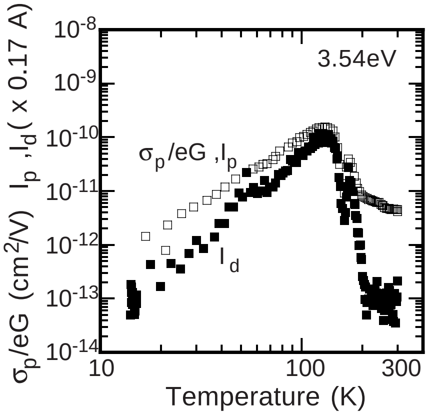

Figure 3. Temperature dependence of normalized photoconductivity σ_p/eG for C_{60} doped PMPS films.

PMPS film. This generation process is denoted by (1) in Fig. 4. For the C_{60} doped PMPS film, as denoted by (2) and (3) in Fig. 4, C_{60} is photoexcited and subsequently an electron transfers from polysilane to C_{60} to leave a hole in the polysilane. In Fig. 4 HOMO and LUMO of C_{60} are assumed to form bands because the optical absorption spectrum shows broad bands.

The corresponding of the low energy onset of the photoconductivity with the absorption edge for the PMPS film indicates that the excess photon energy (being consumed to break excitons) is not required for causing free carriers. However, since our samples have no sandwich structure, the carrier generation process is not the case that the electrode abstracts electrons from migrating excitons. This model was proposed based on the result taken from the samples of a sandwich structure.[7]

Possible processes are a disorder model for molecular materials[9] and a charged-polaron excitation model.[10] In the former the energetic disorder of hopping sites in the polymer matrix lowers the dissociation energy of excitons to make free carriers. In the later, the lowest optical transition in a one dimensional polymer is from the ground state to the relaxed excited state which is the coupling of electrons with distortions in the polymer backbone by the electron-phonon interaction. This photoexcitation yields charged (positive and negative) polarons which promptly contribute to the photocurrent. Our results are not enough to distinguish which models are appropriate for PMPS. We will discuss later the generation process of free carriers based on another disorder model developed in the field of amorphous inorganic semiconductors.[11] It is noted that the concept adopted in the disorder model for the molecular materials is the same as in this model.

The high energy onset of the photoconductivity for the PMPS film appears at photon energy ~0.4 eV higher than the absorption edge and the same onset is observed for the C_{60} doped PMPS film. This onset energy is higher than the peak energy of the absorption, indicating that the large number of charges are photoexcited to the states higher than the DOS peak. According to the disorder models those charges easily become free from the electron-hole pairs.

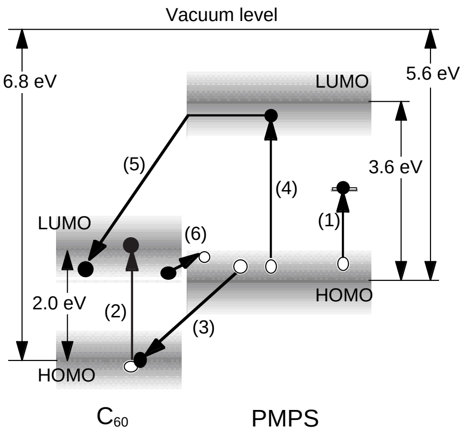

Figure 4. Scheme of photogeneration of carriers and thermalization of trapped charge.

The value of σ_p/eG for the PMPS films is ~ 10^{-12} cm^2/V at T = 15 K where carriers cannot hop up in energy because of the lack of thermal energy. This value is close to the zero temperature photoconductivity estimated for hydrogenated amorphous Si by the disorder model.[11]

We will briefly review the disorder model for amorphous semiconductors. Let us consider an electron-hole pair generated at or just below the mobility edge of an amorphous semiconductor at $T = 0$. The pair is generated quite close together because of the exponential decay their overlap integral with distance. In the analysis the fate of one electron-hole pair is described assuming that the hole is fixed in space. The electron can take part in two competing processes: it can hop down in energy because of $T = 0$ K to a nearest localized state of the tail at distance r with the rate

$$\nu_d(r) = \nu_0 \exp(-2r/a) \qquad (1)$$

or it can recombine with the hole at a rate

$$\nu_r(R) = \tau_0^{-1} \exp(-2R/a) \qquad (2)$$

where R is the electron-hole separation and a is the localization radius of the electron. The prefactor ν_0 is the phonon frequency $\nu_0=10^{12}$ s^{-1} and τ_0 is the typical dipole radiation life time $\tau_0=10^{-8}$ s.

It is clear from Eqs. (1) and (2) that due to strong inequality $n_0 >> \tau_0^{-1}$ diffusion dominates for the first steps. After each hop the average concentration of accessible states decreases and the distances R and r increase. The real competition between recombination and hopping starts only at $R = R_c$, where $R_c = (a/2)\ln(\nu_0\tau_0)$ corresponding to the difference of $r - R$ at $\nu_d = \nu_r$. Thus, the geminate recombination probability is small when $R < R_c$ because diffusion dominates recombination. It reaches a maximum near $R = R_c$ and then decreases with increasing R. The nongeminate recombination which contributes to the photoconductivity appears when R becomes about half the average carrier separation $n_0^{-1/3}/2$ ($> R_c$) where n_0 is the steady state electron (or hole) concentration under the generation rate G at T=0 K. Assuming that the band tails have the DOS with exponential distribution with the width of ε_0, we have the expression of the normalized photoconductivity given by

$$\frac{\sigma_p}{eG} = \frac{e a^2}{12\varepsilon_0} \ln\left(\nu_0 \tau_0\right) L \qquad (3)$$

where $L = n_0^{-1/3}/a$ and is the solution of the equation

$$L = \ln\left[G\tau_0 a^3 L^2 \ln\left(\nu_0\tau_0\right)\right]^{-1} \qquad (4)$$

A reasonable choice of the parameters for amorphous Si gives $\sigma_p/eG=4\text{x}10^{-12}$ cm^2/V which is close to the experimental result of ~10^{-11} cm^2/Vs.

For the PMPS we obtain 10^{-12} cm^2/V from Eq. (3) using L~17 for $G = 10^{19}$ cm^{-3}s^{-1} and the reasonable material parameters $a = 0.53$ nm for a hole (less than the typical electron value of 1 nm), $\varepsilon_0 = 0.04$ eV determined from Fig. 1 and $\nu_0\tau_0 = 10^4$. Furthermore, this theory predicts that the temperature T_r at which the photoconductivity starts to rise (the transport energy crosses the zero-temperature Fermi level) is $3\varepsilon_0/2kL$, where k is the Boltzmann's constant. The parameters for PMPS give $T_r = 41$ K. It can be seen in Fig. 2 that the photoconductivity starts to rise around 40 K, however the sharp rise occurs at 100 K and 200 K. The rise at rather high temperatures has been observed for the case of hydrogenated amorphous SiN.[12] This might be related to the carrier transport properties such as a mobility. The oriented polysilane film which has the lower value of T_r has higher mobility than the unoriented polysilane film.

It has been confirmed that the photocurrent varies in a super linear against the electric field. This can be explained by the electric field distortion not only of the Coulombic potential field between an electron-hole pair but also of the potential relation between nearest hopping sites.

The strange temperature dependence of photoconductivity observed for the C_{60} doped PMPS film is explained as follows. The photogenerated electrons in the polysilane transfer to C_{60} as denoted by (4) and (5) in Fig. 5 and the life time of holes left in the polysilane becomes long because of the spacial separation from electrons. Consequently holes accumulate to move the quasi-Fermi level for holes toward or into the HOMO band and then the dark and photocurrent become larger and larger with time. The measurement was done with increasing the temperature so that the variation from 15 K to 130 K reflects the accumulation of holes. As the temperature rises beyond 130 K, electrons trapped at the lowest level in the LUMO band of C_{60} are thermally excited to recombine with holes in the polysilane as denoted by (6) in Fig. 4, by which the dark current decreases and the ratio of the photocurrent to the dark current becomes large.

We have confirmed that the accumulation of holes is hard by the excitation using the photon energy of 2.25 eV, indicating the process of (3) in Fig. 4 is not effective at a low temperature, although it contributes high photoconduction at room temperature.

Conclusion

The photoconductivity spectrum of PMPS film has an onset coincident with the optical absorption edge and this photoconduction is not due to the hole creation from excitons at electrodes but due to photogeneration of holes in the disorder system or photogeneration of charged polarons. The analysis of the disorder model successfully explains the zero temperature photoconductivity. Doping of C_{60} well sensitizes the photoconductivity of PMPS in the spectral region where C_{60} has optical absorption. This sensitization is suppressed at lower temperature. In a low temperature region holes accumulate by the photoexcitaion of PMPS and the dark and photoconductivity increase. The accumulated holes recombine with electrons in C_{60} at temperatures higher than 130 K.

Acknowledgments

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Biography

Yoshikazu Nakayama received his B.S. in Electric Engineering from Osaka Prefecture University in 1972, and Ph.D. in Applied Physics from Osaka University in 1985. He joined Matsushita Electric Industry Co., Ltd. in 1972 working on holographic memory. In 1979, he moved to Osaka Prefecture University and has worked on solid-state physics, especially photoconductive materials, and plasma processing for semiconductor materials. He was appointed to the position of professor in 1995. From 1992 to 1993 he was the visiting researcher in the James Franck Institute, University of Chicago, Chicago, USA.