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Photoconductivity in fullerene-doped polysilane thin films

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Abstract

Flash photolysis time-resolved microwave conductivity (FP-TRMC) measurements have been performed to study the transport properties of charge carriers in the polysilane films. The effect of C_{60} concentrations on photoconductivity of poly(methylphenylsilane) (PMPS) and poly(*n*-hexylphenylsilane) (PHPS) films has been studied using a variety of excitation light sources. The value of $\phi\sum\mu$, which is the product of quantum efficiency of photocarrier generation (ϕ) and sum of moibilities of the carriers ($\sum\mu$), depends strongly on C_{60} concentration upon exposure of 532 nm. The quantum efficiency reaches ∼0.06 with C_{60} concentration at 5.7 mol%, and saturates at the higher concentrations. The $\phi\sum\mu$ value increases considerably upon exposure of 193 nm up to 1.22×10^{-3} cm^2/Vs without significant dependence on C_{60} concentration, suggesting the direct formation of electron-hole pair by 6.39 eV photon absorption with the higher ϕ value at ∼0.12. The present technique gave the estimates of intra-chain mobility of charge carriers in PMPS and PHPS, and one-order magnitude higher intra-chain mobility was observed in PHPS than that in PMPS. This is suggestive of a highly ordered Si backbone conformation in PHPS. The intra-chain mobility in PMPS, however, is at least two orders of magnitude higher than the mobility values estimated by conventional time-of-flight techniques. Thus we conclude that the higher mobility than $\sim10^{-3}$ cm^2/Vs ($E\sim0$) is realizable even with PMPS by precise synthesis and device fabrication free from disordering, defects, impurities, etc.

Keywords: TRMC; Polysilane; Flash photolysis; Mobility; Charge separation

1. Introduction

Poly(methylphenylsilane) (PMPS) shows photoconductivity and doping of C_{60} in PMPS sensitizes the photoconductivity [1,2].Recent researches have attracted much attention on polysilanes due to significant delocalization of charges along their chains, low cost and easily form films. Amorphous silicon backbone polymers such as PMPS have potential applications in light emitting diodes (LEDs), [3] photoresist, [4] photoconductors, [5] one-dimensional semiconductors, [6–8] low-cost photovoltaic cells, [9] and optoelectronic devices. The studies of photocarrier generation mechanisms and the transport properties in σ-conjugated polymers have still lagged behind.

Fullerene, C_{60}, is an excellent electron acceptor and forms charge-transfer (CT) complexes with a variety of strong donors [10,11]. Enhancement of photoconductivity upon C_{60} doping has also been observed in polysilanes such as PMPS [1,2]. An increase of photocarrier generation yield in polysilanes and optimization of charge carrier mobility are two important parameters for potential application of polysilanes as optoelectronic devices. The doping of C_{60} to polysilanes would suppress the recombination of photo generated charge carriers by assisting the electron transfer from polysilanes [9]. The highest photocarrier generation yield have been observed for fullerene-doped PMPS ($\phi = 40\%$) at an applied field of 100 V/μm upon exposure of 340 nm, and fullerene-doped poly (*N*-vinylcarbozole) ($\phi = 10\%$) at 100 V/μm upon exposure of 340 nm [12].

The electrodeless flash-photolysis time-resolved microwave conductivity (FP-TRMC) [13–17] technique is the best technique over other conventional techniques such as time-of-flight (TOF) or field-effect-transistor (FET) to measure the intrinsic mobility of charge carriers. In the small perturbation regime, the TRMC signal is proportional to the product of the number of charge carriers generated by a laser pulse and their mobility ($\sum\mu$), because the high frequency (∼GHz) of the microwave induces the oscillation of charge carriers with nm-scale displacement. Thus the intrinsic value of $\sum\mu$, which is free from the effects of grain boundaries, impurities, inter-molecular(site) hoppings, can be calculated quantitatively from the TRMC sig-

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nals by an use of the value of ϕ determined by the other techniques without any assumptions.

In the present paper, the effect of concentrations of C_{60} on the photoconductivity of polysilanes using a variety of excitation light sources is discussed by a use of FP-TRMC technique. The value of intra-chain charge carrier mobility reveals the intrinsic nature of Si backbone in polysilanes with different backbone configuration.

2. Experimental

Polysilanes were prepared by the Kipping method using corresponding *n*-alkyl-phenyldichlorosilanes with sodium metal in dry toluene for 5–20 h at 110 °C. The details of the synthesis procedure of the polysilanes were described in the literature [18,19]. Molecular weights of the polymers were measured by a Shimadzu LC-10A gel permeation chromatography system equipped with three Shodex KF-805L columns, and determined relative to polystyrene calibration standards in tetrahydrofuran as an eluent. The number average molecular weights (M_n) were 4.8×10^4 (PMPS) and 1.1×10^6 (poly(*n*-hexylphenylsilane): PHPS), respectively, with their molecular weight distribution (M_w/M_n) less than 2.2. C_{60} (purity 99.95%) was purchased from MTR Ltd., and used as received.

Polysilanes and C_{60} were dissolved separately into *o*-dichlorobenzene at 60 mmol dm^{-3} conc. (base mol unit) and 5 mmol dm^{-3} conc., respectively. Film samples were prepared by drop-casting method onto quartz substrates from the mixed solutions, and dried in a vacuum oven at 55 °C for 2–3 h. Thickness of the films was 1–4 μm measured by Dektak ^{3}ST surface profiler. Absorbance of film samples was measured by Shimadzu UV-3100PC spectrophotometer. Photoluminescence experiments were carried out for the films using Perkin-Elmer LS50B spectrometer.

The films were excited by both excimer and Nd: YAG lasers. The nanosecond laser pulses from excimer lasers [ArF (193 nm: 6.39 eV) and KrF (248 nm: 4.98 eV)] of Lambda Physics, Compex 102, FWHM 5–8 ns) and from Nd: YAG lasers (the third harmonic generation (355 nm: 3.48 eV) and the second harmonic generation (532 nm: 2.32 eV) of Spectra Physics, GCR-130, FWHM 5–8 ns were used as excitation sources. Transient conductivity was measured for the films using TRMC system. The resonant frequency and the microwave power were set at ∼9.1 GHz and 3 mW, respectively, so that the motion of charge carriers can not be disturbed by the low electric field of the microwave in the cavity. The TRMC signal picked up by a crystal diode (rise time < 1 ns) is monitored by a digital oscilloscope (Tektronix, TDS3052B, rise time 0.7 ns). All the above experiments were carried out at room temperature. The transient photoconductivity ($\Delta\sigma$) of a polymer film is related to the reflected microwave power ($\Delta P_r/P_r$) and the sum of the mobilities of charge carriers via

$$< \Delta\sigma > = \frac{1}{A}\frac{\Delta P_r}{P_r} \tag{1}$$

$$\Delta\sigma = N \times e \sum \mu\phi \tag{2}$$

where A, N, e, ϕ and $\sum\mu$ are the sensitivity factor, the number of absorbed photons per unit volume, elementary charge of an electron, photocarrier generation yield (quantum efficiency), and sum of mobilities for negative and positive carriers, respectively.

3. Results and discussion

Photoconductivity of poly(*n*-alkylphenylsilane)s was reported as a function of carbon number of *n*-alkyl group using 532 nm laser pulses as an excitation source in our previous study [21]. For this laser source, TRMC signals have been observed for polysilane samples only after fullerene doping, suggesting that fullerene increases the quantum yield of photocarrier generation. It is important to optimize the concentration of fullerene in polysilane film contributing towards the maximum photocarrier generation. The role of different excitation sources (energy of incident photons) cannot be avoided towards charge carrier generation in the polysilane films.

Fig. 1 shows the dependence of the transient maximum of $\phi\sum\mu$ values observed in PMPS on fullerene concentration upon exposure of 532 nm. In this photon energy, C_{60} molecule excited to singlet state ($^1C_{60}{}^*$) and then converts to $^3C_{60}{}^*$ via intersystem crossing within a few nanoseconds. The yield of triplet state of C_{60} is quite high and lifetime of $^3C_{60}{}^*$ is reported as 10.2 μs [22]. This photon energy is not able to excite polysilane molecule directly. The electron-transfer reaction between ground state of polysilane (PS) and triplet state of fullerene is expected as follows:

$$^3C_{60}{}^* + \mathrm{PS} \rightarrow C_{60}{}^{\cdot -} + \mathrm{PS}^{\cdot +} \tag{3}$$

The $\phi\sum\mu$ value increases linearly with an increase in fullerene concentration in the film, but it levels off at higher C_{60} concentration. The increase in $\phi\sum\mu$ is attributed to an increase in ϕ due to the random-site distribution of C_{60}, changes in the dipole moment of the film, or a contribution from electron mobility on C_{60} (C_{60} aggregates). For the second factor, the decrease in the total dielectric constant induced by doping with C_{60} (with a low dipole moment) often causes an increase in the mobility, but reduces ϕ [23]. The changes in the dipole moment could

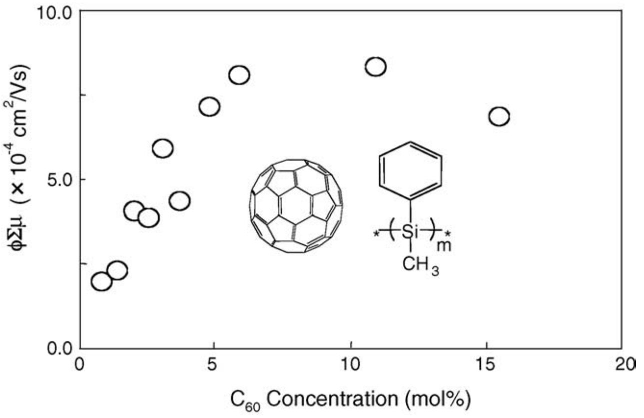

Fig. 1. Dependence of $\phi\sum\mu$ values on fullerene concentrations (mol%) in PMPS films for 532 nm excitation. Inset shows the molecular structures of C_{60} and polysilanes investigated in the present study.