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Photoconduction of (silicon nanocrystals)–(organic polysilane) composites

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Abstract

Photoconduction of thin films of Si nanocrystals (nc-Si) dispersed in poly(methylphenylsilane) (PMPS) matrix prepared by printing has been studied by means of steady-state photoconductivity and time-of-flight (TOF) transient photocurrent measurements. Addition of nc-Si whose average diameter is 27 nm to PMPS induces photoconductive response in a visible spectral range from 1.9 to 3.35 eV, where no photoconductive response is observed in pristine PMPS. The dark current–voltage, steady-state photoconductivity and TOF measurements indicate that the roles of nc-Si and PMPS in nc-Si/PMPS composites are photocarrier generation and photocarrier transport, respectively. The TOF transient photocurrent measurements reveal that the hole drift mobilities of the composite are essentially unaffected in the nc-Si concentration range from 0 to 5 wt.% but nc-Si addition increases energetic disorder. The increase in energetic disorder is attributable to surface states of nc-Si.

Keywords: Photoconduction; Si nanocrystals; Polysilane; Drift mobility

1. Introduction

High-molecular-weight silicon (Si) backbone polymers, polysilanes, are currently receiving considerable research attention because of their unique nonlinear optical [1], photostructural [2] and photoelectric properties [3–5]. Polymethylphenylsilane (PMPS) is regarded as a prototypical amorphous polysilane.

Optical properties of Si nanocrystals (nc-Si) have attracted much attention because of visible photoluminescence from the materials at room temperature due to quantum confinement effects [6]. In addition, the photoconductive properties of nc-Si have been observed [7,8]. By dispersing semiconductor nanocrystals in polymers, an interesting class of photoconductive nanocomposites is fabricated [9,10] For devices based on the use of dispersed nanocrystals in polymers, there is considerable interest for low cost manufacturing using simple solution coating or printing techniques.

In this work, photoconduction of printed thin films of nc-Si dispersed in PMPS is studied in terms of steady-state photoconductivity and time-of-flight (TOF) transient photocurrent measurements. We will show that photoconductive response in a visible spectral range, which is not observed in pristine PMPS, is observed in nc-Si/PMPS composites. The role of nc-Si and PMPS in the composites, and the influence of nc-Si addition to transient hole transport properties of PMPS will be discussed.

2. Experimental

The molecular weight of PMPS was evaluated to be 110 000 by gel permeation chromatography and their synthesis has been described in literature [2]. nc-Si used in this work was produced by a laser breakdown method of silane (SiH_4) gas. The nc-Si was oxidized at room temperature in a clean-air box. A transmission electron microscopy examination indicates that the oxidized Si nanocrystallites consist of a c-Si core and SiO_2 surface layer [6]. The distribution of the overall diameter of

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these nanocrystallites can be described by a log-normal function:

$$dF(D) = \frac{1}{D\sqrt{(2\pi\sigma^2)}} \exp[-(\ln D - \mu)^2/2\sigma^2]dD \quad (1)$$

where D is the average diameter, σ and μ are shape and scale parameters, respectively. The average diameter of nc-Si was calculated to be 27 nm. For the optical absorption and photoluminescence spectra measurements, samples were prepared by spin-coating technique from a tetrahydrofuran solution of PMPS and nc-Si onto quartz substrates. Samples for the steady-state photoconductivity spectra measurements and the time-of-flight (TOF) measurements were coated onto indium–tin–oxide (ITO) precoated glass substrates by wire-bar technique, and gold electrodes were then vacuum deposited on top of the composite films. The sample thickness ranged from 1 to 3 μm. The optical absorption spectra and the photoluminescence spectra of the thin films were measured with a Shimadzu UV-3100PC scanning spectrophotometer and a Shimadzu RF-5300PC spectrofluorophotometer, respectively. For the steady-state photoconductivity spectra measurements, the light passed through a monochromator from a halogen lamp was irradiated though the ITO electrodes. The signal derived from a silicon photodiode was fed to a lock-in amplifier and the resulting photoconductivity spectra were normalized to the equal number of incident photons. Transient photocurrent of the samples was studied by the TOF technique that permits the measurement of charge carrier mobility and by choosing the polarity of electric field applied to the samples, electron and hole transport can be studied separately. The light sources for the transient photocurrent measurements were 10 ns light pulses of 337 nm from a nitrogen laser and 470 nm radiation from a nitrogen laser pumped dye laser. The current passing through the samples was monitored with a digital oscilloscope.

3. Results

3.1. Optical absorption, photoluminescence and photoconductivity spectra

Fig. 1 shows the optical absorption spectra of nc-Si in polyester (20 wt.% nc-Si), PMPS and 20 wt.% nc-Si/PMPS composite films. The one-dimensional exciton absorption peak of PMPS at 3.7 eV is observed along with the characteristic nc-Si absorption over spectral range from 1.0 to 3.1 eV in the nc-Si/PMPS composites. The absorption spectra of the nc-Si/PMPS composite films are a simple superposition of the two components without any indication of significant interaction between

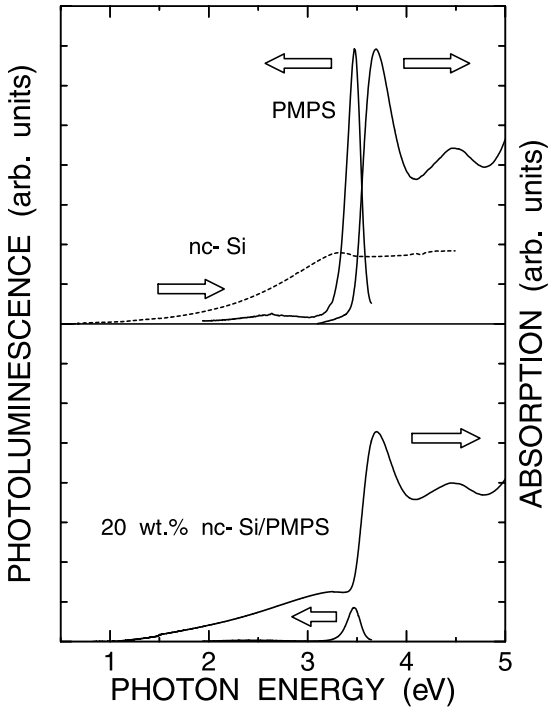

Fig. 1. Optical absorption and photoluminescence spectra of PMPS thin films (upper figure). Optical absorption spectrum of 20 wt.% nc-Si/polyester composite is also shown as the dashed line in the upper figure. Optical absorption and photoluminescence spectra of 20 wt.% nc-Si/PMPS composite thin films (lower figure). All the measurements were carried out at 295 K.

the two materials in the ground state. We also show the photoluminescence spectra of PMPS and nc-Si/PMPS composites in Fig. 1, and find that the photoluminescence intensity is reduced with nc-Si dispersed in PMPS.

Fig. 2 shows the photoconductivity response of nc-Si/PMPS composites, which is enhanced with increasing nc-Si concentration over spectral range from 1.9 to 3.8 eV. Addition of 2 wt.% nc-Si to PMPS induces photoconductivity response in a visible spectral range from 1.9 to 3.35 eV, and further nc-Si addition (20 wt.%) to PMPS increases photoconductivity at 2.52 eV by about 20 times. The experimental results in Fig. 2 demonstrate the sensitization in visible spectral range of PMPS by nc-Si addition.

3.2. Time-of-flight measurements

Hole transient photocurrents of PMPS and nc-Si/PMPS composites (2 and 5 wt.% nc-Si) excited by 337 nm light pulse at 292 K were illustrated in Fig. 3(a–c), respectively. No hole transit signals were observed for >5 wt.% nc-Si/PMPS composites. It can be seen from the figures that the transit-time dispersion increases with increasing nc-Si concentration. The transit times of holes are identified by a peak or a shoulder of the current, characteristics of nondispersive transport, and thus their drift mobilities are calculated from the transit

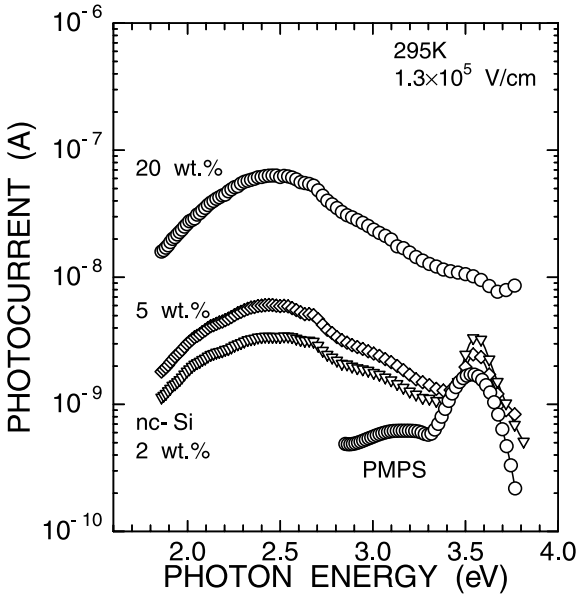

Fig. 2. Photoconductivity spectra of PMPS and 2, 5, 20 wt.% nc-Si/PMPS composite thin films. All the measurements ware carried out at 295 K.

times via the relationship, $\mu_d = L/t_r F$, where μ_d is the drift mobility, L is the sample thickness, t_r is the transit time, and F is the applied electric field. The drift mobilities of the nc-Si/PMPS composites at 292 K are almost independent of nc-Si concentration (0–5 wt.% nc-Si).

The temperature and electric field dependences of hole drift mobilities are shown in Fig. 4(a–c), and fit the Gill's empirical expression of the form [11],

$$\mu_d = \mu_0 \exp\left[-\frac{E_0 - \beta\sqrt{F}}{kT_{eff}}\right] \quad (2)$$

where $1/T_{eff} = 1/T - 1/T_0$, μ_0 is the mobility at $T = T_0$, E_0 is the zero field activation energy, β is a constant, and T_0 is the temperature at which extrapolated temperature dependences at different fields intersect. The physical quantities obtained from the fitting are shown in Fig. 5. With increasing concentration of nc-Si in nc-Si/PMPS composites, μ_0 remains almost constant, but E_0 becomes larger.

The sensitization in visible spectral range of PMPS by nc-Si addition enables us to excite TOF photocurrent transients by 470 nm light pulses (no hole transient signal of pristine PMPS was observed at this excitation wavelength). Fig. 6 shows TOF hole photocurrent transients of 2 wt.% nc-Si/PMPS at 292 K for different applied electric fields. The photocurrent transients excited by 470 nm light pulses are similar to those by 337 nm light pulses. Fig. 7 shows the temperature and electric field dependences of hole drift mobilities determined from photocurrent transients of 2 wt.% nc-Si/PMPS excited by 470 nm light pulses. The temperature and electric field dependences in Fig. 7 are almost the same as those measured by 337 nm excitation shown in Fig. 4(b).

4. Discussion

The sensitization of PMPS in a visible spectral range has been observed by nc-Si addition to PMPS. We examine the roles of nc-Si and PMPS in the photoconductivity response in such composites by carrying out an additional experiment, the nc-Si concentration dependence of dark conductivity of nc-Si/PMPS estimated from the Ohmic region of dark current (I)–voltage (V) characteristics, using a percolation approach [8,12]. The dark conductivity σ_d is found to drastically increase above a threshold value, p_c, with increasing nc-Si concentration [8]. Under percolation conditions, for p above the critical concentration p_c, the conductivity scales in the vicinity of p_c:

$$\sigma_d = \sigma_0(p - p_c)^{\gamma} \quad (p > p_c) \quad (3)$$

and $\sigma = 0$ ($p < p_c$), where γ is the conductivity exponent. The conduction path under the condition of Eq. (3) is formed by nc-Si clusters in PMPS matrix. The best overall fit to the data gives $p_c = 9.4$ wt.% [8]. Therefore, it is likely that the increase in the photoconductivity response results from the hole transfer from nc-Si to PMPS and subsequent hole transport in PMPS matrix in nc-Si/PMPS (2 and 5 wt.% nc-Si) (below p_c, the roles of nc-Si and PMPS are photocarrier generation and photocarrier transport, respectively), while in 20 wt.% nc-Si/PMPS composites, photocarrier transport in nc-Si percolation clusters as well as in PMPS occurs, which leads to drastic increase in photoconductivity, as found in Fig. 2. The increase in photoconductivity in nc-Si/PMPS is consistent with photoluminescence quenching in Fig. 1.

The interpretation described above is consistent with the results of the TOF experiments. The hole drift mobilities and the values of μ_0 derived from the analysis based on Eq. (3) of nc-Si/PMPS composites in the concentration range of 0–5 wt.% nc-Si are almost constant, indicating that the hole transport path in the composites is in PMPS matrix.

Addition of nc-Si to PMPS does not strongly influence the values of μ_0 but increases the zero-electric field activation energy of hole drift mobilities of the composites with increasing nc-Si concentration. The increase in the activation energy may result from the increase in energetic disorder. This has been confirmed by both space-charge-limited current and steady-state photoconductivity measurements [8], from which we found that the localized-state distributions in nc-Si/PMPS composites become broader with increasing nc-Si

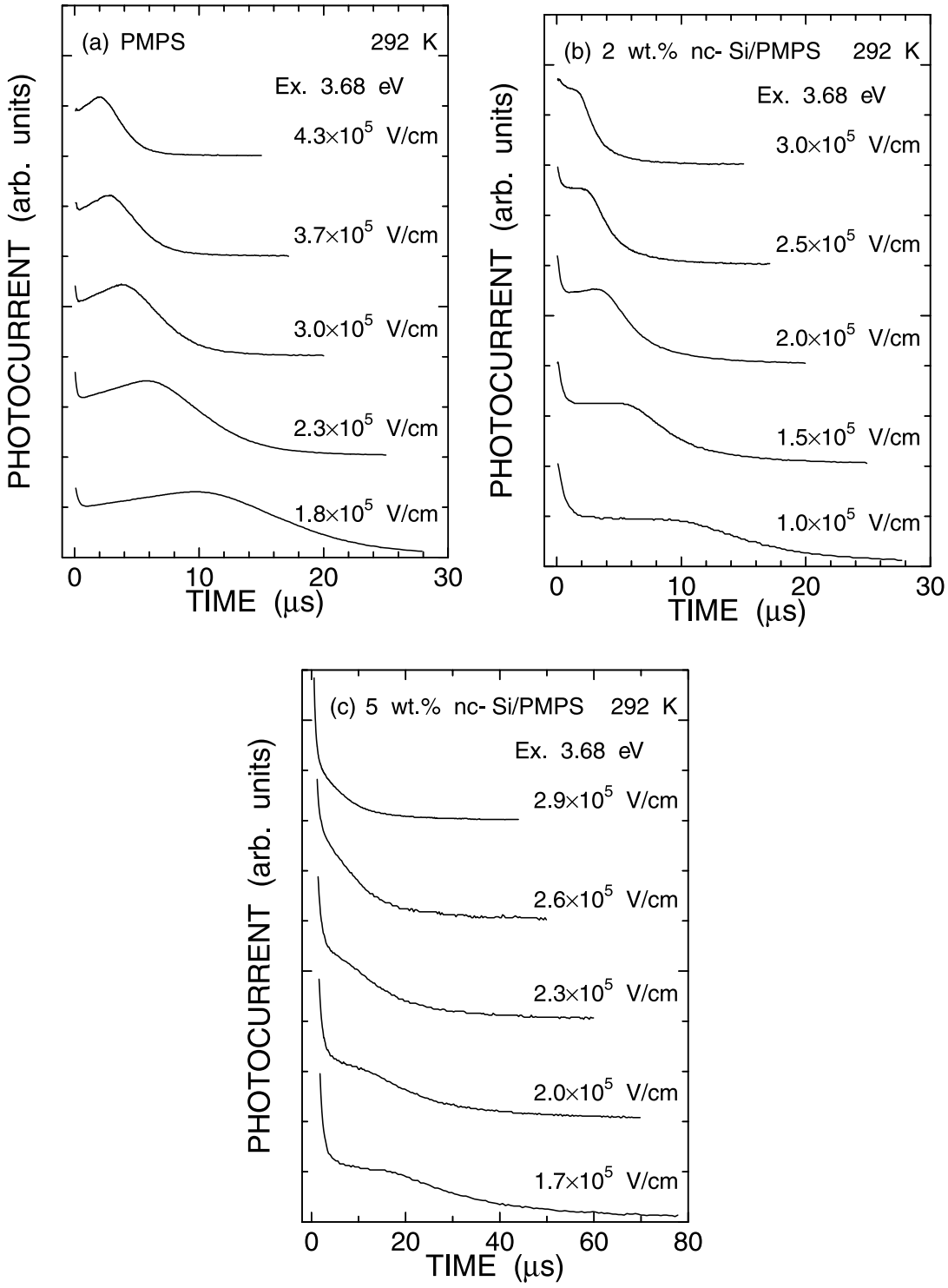

Fig. 3. TOF transient hole photocurrent signals, excited by 3.68 eV light pulses, of PMPS ($L = 1.6$ μm) (a), 2 wt.% nc-Si/PMPS ($L = 2.0$ μm) (b) and 5 wt.% nc-Si/PMPS ($L = 3.5$ μm) (c) at 292 K. TOF measurements for these three samples were carried out for different electric fields, 1.8×10^5–4.3×10^5 V cm^{-1} (a), 1.0×10^5–3.0×10^5 V cm^{-1} (b) and 1.7×10^5–2.9×10^5 V cm^{-1} (c).

concentration, consistent with the increase in the activation energy of hole drift mobilities. The results are also consistent with the increase in the transit-time dispersion, observed in Fig. 3, with increasing nc-Si concentration.

We have also found that the localized states originate in the surface states of nc-Si [8]. Thus, to reduce the density of surface states in nc-Si and thereby to improve the photoconductive properties of nc-Si/PMPS composites, the chemical modification of nc-Si surfaces is

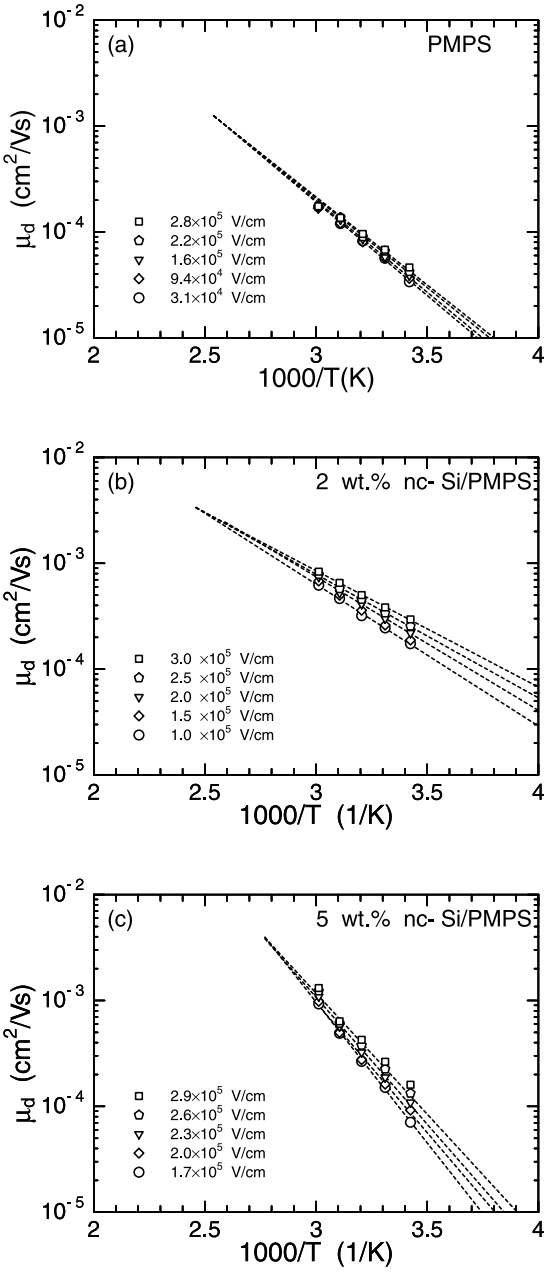

Fig. 4. Temperature and electric field dependences of hole drift mobilities of PMPS (a), 2 wt.% nc-Si/PMPS (b) and 5 wt.% nc-Si/PMPS (c). The dashed lines are the best-fitted lines of Eq. (2).

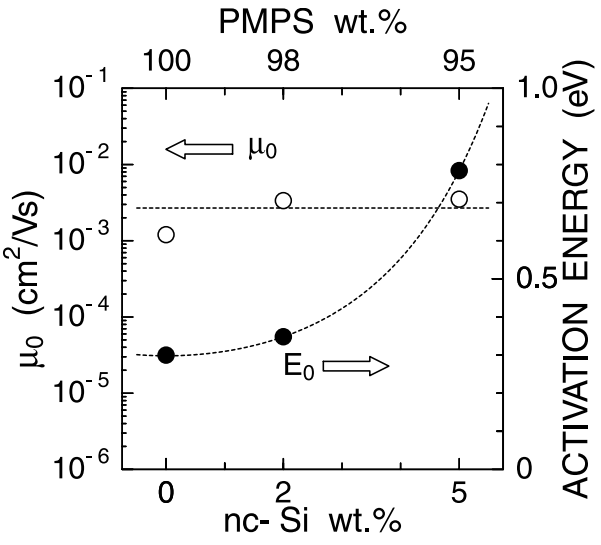

Fig. 5. Hole transport parameter [μ_0 and E_0 in Eq. (2)] of PMPS, 2 wt.% nc-Si/PMPS and 5 wt.% nc-Si/PMPS, obtained from the fitting of the Gill's experimental expression to the experimental data.

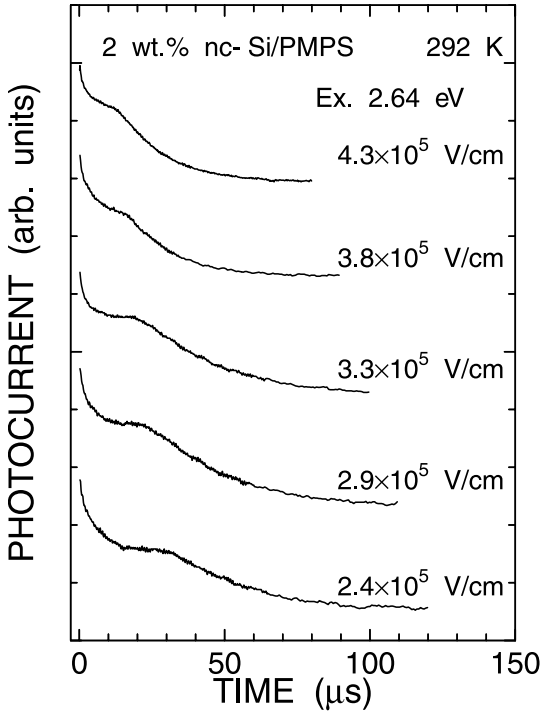

Fig. 6. TOF transient hole photocurrent signals, excited by 2.64 eV light pulses, of 2 wt.% nc-Si/PMPS ($L = 2.0$ μm) at 292 K.

essential. In addition, a method for measuring the surface-state distributions in nc-Si would be important to monitor the effect of chemical modification of nc-Si surfaces. For this purpose, an analysis of photocurrent transients of nc-Si/PMPS composites is suitable [13,14], and will be published elsewhere.

Although the reduction of surface-state density of nc-Si is an important issue for potential application of nc-Si/PMPS composites to photoelectric devices, the dispersion of nc-Si in PMPS matrix is an promising approach for sensitization of PMPS in a visible spectral range as well as the utilization of excellent transport properties of PMPS. As shown above, nc-Si and PMPS act as photocarrier generation sites and photocarrier transport path, respectively, in nc-Si/PMPS composites below the percolation threshold of nc-Si. Thus, for instance, by doping narrow-gap semiconductor nanocrystals such as InAs and PbS in PMPS, we can obtain infrared-sensitive photoconductors.

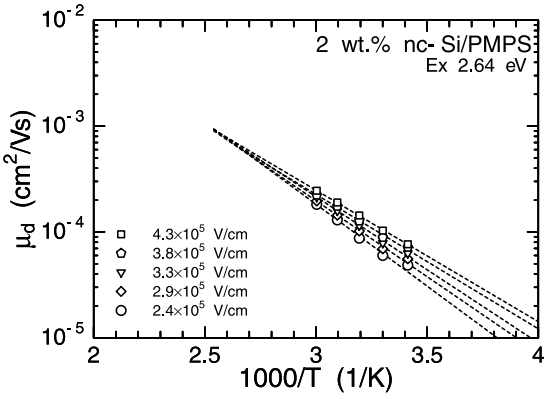

Fig. 7. Temperature and electric field dependences of hole drift mobilities of 2 wt.% nc-Si/PMPS. The dashed lines are the best-fitted lines of Eq. (2).

5. Conclusions

We have studied photoconduction of nc-Si/PMPS composites in terms of steady-state photoconductivity and TOF photocurrent transients. It is found from the steady-state photoconductivity experiments that photoconductive response of the composites in a visible spectral range from 1.9 to 3.5 eV, where no photoconductive response is observed in pristine PMPS, is induced by nc-Si addition. The nc-Si concentration dependence of dark conductivity is well described by a percolation theory, and the percolation threshold is found to be 9.4 wt.%. The TOF measurements using 337-nm excitation show that the hole drift mobilities of the composites are almost unaffected by 0–5 wt.% nc-Si addition, while the zero-field activation energies of the hole drift mobilities increase with increasing nc-Si concentration. The TOF transient photocurrent of the composites is also observed by 470 nm excitation. We find from these experiments that the roles of nc-Si and PMPS are, respectively, photocarrier generation and photocarrier transport in the composites. The increase in the activation energy is due to the increase in energetic disorder resulting from the surface states of nc-Si.

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